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THE PURIFICATION OF COPPER SULPHATE SOLUTIONS

BY

GEORGE S. TILLEY and OLIVER C. RALSTON

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THE PURIFICATION OF COPPER SULPHATE SOLUTIONS

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INTRODUCTION

One of the main deterrents to the use of sulphuric acid leaching and electrolysis for extracting copper from its ores has been the fouling of the solutions with soluble impurities of the ore—especially iron and, to a minor degree, aluminum. Any simple, inexpensive means of removing these two impurities, with any other impurities that might tend to accompany them, would not only be of value in copper leaching but also in copper refining, in purifying bluestone-plant solutions, and in treating mine water that contains copper. This paper deals largely with that problem. Much work has been done in the past, but on investigation it was found that the subject had not been adequately discussed and the references to it were scattered widely. A review of past work is given below to show what progress has been made toward solving the problem, and a report on the investigations made by the Bureau of Mines follows.

The removal of iron and aluminum, and, to a less extent, silica, from copper solutions is closely related to the similar problem in the purification of zinc sulphate solutions by electrodeposition of zinc. The problem of removing ferrous and ferric iron is likewise closely related to the purification of aluminum sulphate solutions for the manufacture of alums, or of aluminum oxide for the manufacture of metallic aluminum. Hence, much previous research, particularly with regard to the purification of zinc solutions, applies to this investigation, and many theoretical data are identical.

The authors therefore proposed:

1. To collect data on past work from literature, from operating companies, and from consulting metallurgists.

2. To study in commercial practice the influence of temperature, degree of agitation, and concentration of solution on the order and rate of precipitation of impurities in copper sulphate solutions by such reagents as limestone, milk of lime, copper oxide, and native copper ores.

3. To remove ferrous iron from solutions by oxidation, by aeration under various conditions, or with catalytic or direct oxidizing agents.

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This procedure is of prime importance whenever purification of copper sulphate solutions or zinc or aluminum sulphate solutions is desirable. This was studied in great detail.

4. To investigate the character of precipitates formed, with reference to commercial filtration and washing or thickening, and with reference to working up mixed precipitates, if obtained.

5. To develop practical procedure for the purification of solutions.

PREVIOUS WORK ON PURIFICATION OF COPPER SULPHATE SOLUTIONS

GREENAWALT'S REVIEW OF EARLY PROCESSES

Greenawalt[1] reviews early experiments on the purification of copper sulphate solutions and also describes certain processes separately in his "Hydrometallurgy of Copper."

MILLBERG PROCESS

The Millberg process[2] probably works out the purification of copper sulphate solutions in more detail than many other processes do, although it was not reported in full by Greenawalt. This process, now used in several European plants, was devised after some years of research on the utilization of pyrite cinder containing copper, zinc, manganese, nickel, and cobalt, in addition to the usual sulphur and iron.

Millberg found that ferrous sulphate can be oxidized to ferric sulphate and basic ferric sulphate. The latter precipitates out after aeration from two hours to two days in the complex solutions obtained by leaching pyrite cinder, if the solution is first neutralized by the addition of enough milk of lime just to begin precipitation of copper. Aluminum salts precipitate at the same time. Copper, manganese, nickel, cobalt, and zinc remain in solution if the milk of lime is added in the correct proportion; and they are separated by further selective precipitation from the filtrate from the removal of iron and aluminum. Millberg discovered that ferrous iron oxidized best in dilute solution (not stronger than 18° to 20° B.) Aeration at 35° to 40° C. usually removed all the iron from their solutions within four to six hours. The precipitate of calcium sulphate and basic sulphates of iron and aluminum always contained a small amount of entrained copper, which was removed by treatment of the precipitate with a small amount of dilute acid, forming a little ferric sulphate. The ferric sulphate in turn dissolved the precipitated copper and the resulting solution of ferrous and cupric sulphates returned to the oxidation tank. In a later paper[3] Millberg says that to get better results in filtering the precipitate of basic sulphates, the concentration of the milk of lime, the rate at which lime is added to the solutions, and the temperature of the solution are particularly important. He also advises keeping the solutions at 40° to 50° C.

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[1] Greenawalt, W. E., Hydrometallurgy of copper. 1912, pt. 2, pp. 300–303; on the Hofmann process, p. 444; on the Rio Tinto process, pp. 205–212; on the Millberg process, pp. 202–203.

[2] Millberg, Karl, Kupfer-vitriolgewinnung aus Kiesabbränden und minderwertigen Kupfererzen: Chem. Zeit., Jahrg. 30, 1906, pp. 511–513.

HOFMANN PROCESS

Greenawalt discusses the process of Ottokar Hofmann[4] as used at Argentine, Kans. In this process the copper sulphate solution, containing copper, iron, antimony, and arsenic, is neutralized by roasted copper matte at 75° to 80° C., and then aerated in a special tank. In three to four hours the solution is said to be entirely free from iron, arsenic, antimony, and other impurities, the ferrous iron oxidizing and the ferric precipitating as ferric oxide.[4]

A modification of this procedure is mentioned by Greenawalt as having been used at Anaconda,[4] possibly in one of the early refineries. The copper sulphate solution is repeatedly passed through a layer of oxidized copper, where the antimony and bismuth are partly precipitated. The solution also becomes nearly neutral and saturated with copper. It is then oxidized by aeration and the ferric iron is partly precipitated as ferric oxide. Laist and Maguire[5] in discussing the 2,000-ton leaching plant at Anaconda, state that no purification of solutions was attempted and that "the concentration at which to begin discarding solutions is when the returning solution shows about 0.09 gram per cubic centimeter of $Fe_2O_3+Al_2O_3$." This plant was built and operated after Greenawalt's book was written.

Greenawalt[6] quotes Ulke's "Modern Electrolytic Copper Refining,"[7] in describing the process for purifying copper sulphate solutions at the Kalakent copper works in Russia. There the copper sulphate solutions are first neutralized by heating them, passing them over fine roasted copper matte, and trickling them over heaps of roasted low-grade copper ore; then they are diluted to 12° or 10° B. with wash waters, heated to 50° C., and aerated to remove iron, arsenic, tin, and bismuth. Anode scrap is suspended in the lead pans used for the aeration, to neutralize any remaining part of the acid and to take up any new acid set free by the formation of ferric oxide. This procedure was said to reduce the impurities to 5 or 10 grams of iron a liter, with traces of zinc, cobalt, and nickel.

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[3] Millberg, Karl, Abröstung und Extraktion von kupferhaltigen Kiesabbränden ohne chlorierende Röstung: Chem. Zeit., Jahrg. 31, 1907, pp. 1143–1145.

[4] Greenawalt, W. E., Hydrometallurgy of copper. 1912, pt. 2, on Hofmann process, pp. 301, 434–466; on precipitation of ferric oxide, pp. 441–442; on process at Anaconda, p. 300.

[5] Laist, Frederick and Maguire, H. J., The 2,000-ton leaching plant at Anaconda: Min. and Sci. Press., vol. 116, 1918, pp. 365–370.

[6] Greenawalt, W. E., work cited, pp. 300–301.

[7] Ulke, Titus, Modern electrolytic copper refining. 1903, p. 145.

The Hofmann process as described above was used at the plant of the Consolidated Kansas City Smelting & Refining Co. at Argentine, Kans., for purifying copper sulphate solutions used in the manufacture of bluestone. The same process was later used at the plant of the American Smelting & Refining Co. at Perth Amboy, N. J., under direction of C. S. Witherell, formerly superintendent of the plant at Argentine, Kans., to purify copper sulphate solutions used for refinery electrolyte. Mr. Witherell[8] states that at the Chuquicamata plant of the Chile Exploration Co., where he was "superintendent of reduction," the bulk of solutions is too enormous and fuel is too expensive for advantageous use of the Hofmann method. The small amount of iron deposited electrolytically or mechanically on the copper cathodes is easily scorified out in the cathode melting furnaces. Mr. Witherell mentions a fact observed by the authors, that much cuprous oxide was present in the ordinary roasted copper matte or cement. Its effect while roasted matte or cement is being used to neutralize copper sulphate solutions in the Hofmann process is to reduce ferric to ferrous iron in the solution until the cuprous oxide is entirely oxidized. Metallic copper has the same effect.

OTHER INVESTIGATIONS.

A number of investigations and reports on the purification of copper sulphate solutions have been published since Greenawalt's book appeared.

WORK OF POPE AND HAHN

Pope and Hahn investigated the purification of copper sulphate solution experimentally[9] and on a large scale at Ajo.[10] In their experimental work they followed the Hofmann method, using roasted cement copper, roasted high-grade sulphide copper ore, and roasted copper sulphide concentrates, and high-grade copper carbonate ore as sources of copper oxide. They found that the copper oxide must be ground very finely (93 per cent through a 200-mesh screen). When the copper sulphate solution was purified it was first heated to 195° to 200° F. and maintained at about 195° F. during the run; air agitation was used. The runs lasted about three and one-half hours. All the ferric iron was precipitated during the first hour. At the end of a run 90 per cent of the total iron, 65 to 75 per cent of the alumina, 50 per cent of the manganese, and all of the antimony, arsenic, and bismuth were precipitated. The precipitate filtered easily, and the filter cakes were firm. washed well, and retained only a small amount of unused copper.

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[8] Witherell, C. S., Private communication, Feb. 27, 1922.

[9] Ricketts, L. D., Some problems in copper leaching: Trans. Am. Inst. Min. Eng. vol. 52, 1915, pp. 737–764.

[10] Morse, H. W., and Tobelmann, H. A., Leaching tests at New Cornelia: Trans. Am. Inst. Min. Eng., vol. 55, 1916, pp. 830–955.

In large-scale runs with the Pope-Hahn process[11] in the 40-ton experimental plant at Ajo, about 40 pounds of roasted Miami concentrate (40 per cent Cu) per ton of ore leached was enough to remove impurities satisfactorily. Ninety-two per cent of the copper in the concentrate was recovered. The writers say "Working the Pope-Hahn process would have required the installation of roasting plant, fine-crushing plant, agitators and filter presses, and the purchase of high-grade sulphide ore or concentrates. It offered decided advantages, among them a practically pure solution for electrolysis, together with the regeneration of a high percentage of the acid necessary for leaching." They add that "Results of the Pope-Hahn process were very satisfactory."

METHOD USED IN JAPAN

At the Ashio copper mine of the Furukawa Mining Co., in Japan, the mine waters are purified by a method similar to those described in this paper.[12] The Japanese Government requires the removal of iron as well as copper from the mine water before discharge, because the water from the river is used for irrigation. The mine water is run through three settling ponds. Sand and some slime settle in the first, and coagulated material carrying some copper and slime high in silica in the second and third. In a fourth pond a small quantity of milk of lime (from 10 to 20 per cent of the whole amount necessary for complete neutralization and precipitation) is added, causing precipitation of hydrated iron oxide with a little copper, also alumina and silica; in a fifth pond more lime is added, precipitating the remaining copper which settles here and in a sixth pond. The precipitate is then dried and sent to the smelter.

CORBOULD AND BURBIDGE PROCESS

Purification of copper sulphate solutions was worked out by Corbould[13] and Burbidge[14] as part of a complete plan of treatment of the copper ore at Mt. Elliott, Queensland, Australia. The roasted ore is leached with sulphuric acid, and the liquor neutralized with slimed calcium carbonate and ferrous iron oxidized by aeration in a cone-bottomed tank. Most of the iron is precipitated in this treatment, and the pulp is filtered. The iron remaining in the filtrate is removed by treatment with CuO as in the Hofmann method and the precipitate is returned to the furnace bins for roasting with the next charge to save any entrained or unused copper. The wash liquors are purified separately, calcium carbonate being used in a first neutralization; then they are aerated as before, when the filtrate is treated a second time to obtain the iron not removed by the first treatment; milk of lime is used instead of CuO, the milk of lime being added gradually "to produce as near as possible a 'selective' action—that is, to precipitate most of the remaining Fe with very little Cu." The two calcium sulphate residues containing precipitated basic ferric sulphates and some copper are extracted by dilute ammonia solution, and after the liquid is filtered off from the residue the copper is precipitated from the ammoniacal solution as CuO by distilling off the ammonia.

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[11] Pope, T. A., and Hahn, A. W., Process of Pope and Hahn: Trans. Am. Inst. Min. Eng., vol. 55, 1916, p. 832.

[12] Richards, W. J., Treatment of mine water from the Ashio copper mine: Trans. Am. Inst. Min. Eng., vol. 43, 1912, pp. 464–467; Greenawalt, W. E., Hydrometallurgy of copper. 1912, pt. 2, p. 414.

[13] Corbould, W. H., and Burbidge, Percy, Corbould's copper extraction process: Min. Mag., vol. 25, 1921, pp. 381–385.

[14] Burbidge, Percy, A proposed copper-metallurgical process: Proc. Aus. Inst. Min. Met., vol. 42, 1921, pp. 1–14.

Carbould and Burbidge say "on account of the Fe in the electrolyte being maintained below 0.2 per cent (2 grams per liter), it is possible to use graphite anodes, yielding about 3 pounds of Cu per kw. h. with a current density of 12 amperes per square foot."

WORK OF DU FAUR

Du Faur,[15] also working in Australia, has experimented with the purification of copper sulphate solutions in connection with hydrometallurgical research on copper. Du Faur considers a certain amount of Fe and Al in the electrolyte absolutely necessary for successful electrodeposition of Cu, the iron as ferrous sulphate for depolarization and the aluminum as aluminum sulphate to reduce the corrosive effect of ferric sulphate on the cathodes. Du Faur says that to control the amount of Fe and Al in the solution by precipitating these impurities by CuO alone from part of the solution daily will require an unreasonable amount of CuO and return an excessive amount of acid to the cycle. He proposes to add enough CuO in neutralizing the electrolyte to be purified to return the acid lost when the solution is discarded and to use limestone to precipitate Fe, after ferrous is oxidized to ferric iron by aeration in the presence of manganese dioxide. Du Faur finds that only 43 per cent of the stoichiometrically required manganese dioxide is enough for complete oxidation of ferrous iron with aeration. This manganese is recoverable from the electrolytic cells, where it is deposited on the anode as manganese dioxide and falls into the cell as sludge. In his paper Du Faur works out a complete material flow sheet for a hypothetical mill treating 100 tons of ore a day, by the above method of purification of the electrolyte, the ore having 2.50 per cent of Cu, 15.00 per cent of Fe, and 3.00 per cent of Al after roasting.

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[15] Du Faur, B., Hydrometallurgical research: Chem. Eng. Min. Rev., vol. 12, 1920, pp. 241–244.

WORK OF HICKEY AND McIVER

Hickey and McIver[16] studied the purification of copper chloride and copper sulphate solutions. They tried the effect of adding different amounts of calcium carbonate to solutions containing ferrous and ferric iron, copper and zinc, and sometimes nickel. They conclude that iron can not be eliminated entirely from copper sulphate solutions without a prohibitive loss of copper in the precipitate at room temperatures, although they find that a quantitative separation of iron, copper, and nickel from copper chloride is possible, with all the ferric iron precipitating before the copper or nickel precipitates. Hayward's paper[17] may be mentioned in this connection, because of similar laboratory and large-scale technique and similar results.

PATENTS COVERING PURIFICATION OF COPPER SULPHATE SOLUTIONS

The purification of copper sulphate solutions has been, more or less indirectly, the subject of several patents. For example, U. S. Patents[18] 913,708 and 913,709, of March 2, 1909, issued to H. H. Dow and W. S. Gates, describe the separation of iron, copper, and nickel from solution and in solution by the addition of enough calcium carbonate and milk of lime to precipitate first iron with traces of copper and nickel, and then to separate nickel from copper by precipitating copper and leaving nickel in solution. The patent also describes the principle of purifying the precipitates formed—by long agitation with the liquor from which they were precipitated. For example, the copper and nickel traces precipitated with the first iron precipitate, and the nickel traces precipitated from the second solution with the main copper precipitate redissolve if agitated with the solutions.

Vadner[19] has patented two processes. One covers the removal of iron from solutions obtained by leaching copper sulphide ores with

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[16] Hickey, J. H., and McIver, R. W. E., The differential precipitation of metals from complex leach solutions. Thesis, Massachusetts Inst. Tech. 1922.

[17] Hayward, C. R., Extraction of nickel and alumina from Cuban ores: Chem. and Met. Eng., vol. 26, 1922, pp. 261–266.

[18] Dow, H. H., and Gates, W. S., Process of separating metals in solution, U. S. Patents 913,708 and 913,709, Mar. 2, 1909.

[19] Vadner, C. S., Process for the treatment of copper ores and the recovery of their values, U. S. Patent 1,111,874, Sept. 29, 1914; Process for the recovery of metals from ores and the like, U. S. Patent 1,146,373, July 13, 1915.

NaCl solution and SO_2, treating the solution while hot with finely powdered calcium carbonate and later precipitating copper from the cooled solution by adding more calcium carbonate, aerating the solution each time. The other patent covers the removal of iron from similarly obtained solutions by taking out SO_2 with heat, steam, or air; the solution is then partly neutralized with calcium carbonate and treated with air to partly precipitate the iron as ferric oxide. The filtrate is further neutralized and aerated to complete precipitation.

REDUCTION OF FERRIC IRON TO FERROUS STATE

In a certain sense the control of ferric iron in copper sulphate leach-solutions by reduction to the ferrous condition is a purification of the solution. The various processes that utilize SO_2 gas and pyritic filters may be cited as examples. SO_2 gas was used at Ajo [20] and in the Pechey process employed at the Girilambone, Mount Hope and Whim Well copper mines, Australia.[21] Pyritic filters have been used at Rio Tinto [22]; at Whim Well, Australia, in Sleeman's modification of the Pechey process [23]; and in Spain, Australia, and in the United States by Irving.[24] The present investigation is, however, more concerned with processes in which the impurities are separated from the solution as precipitates.

PRELIMINARY WORK OF BUREAU OF MINES

The preliminary work in this investigation outlined on page 1 was begun by W. C. Riddell and T. S. Chen,[25] in the Bureau of Mines laboratory at Berkeley, Calif. They experimented with the action of 40, 60, and 80 mesh limestone on solutions of ferrous sulphate alone; on copper sulphate and ferrous sulphate together; and on copper sulphate, ferrous and ferric sulphates together, at 14° and 70° C., with and without aeration. From the limited number of experiments possible within the time available they drew the following conclusions:

1. Ferrous iron is not precipitated by limestone if the solutions are kept free from air.
2. An appreciable amount of iron is not precipitated from ferrous solutions upon aeration, in the absence of added alkali.

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[20] Morse, H. W., and Tobelmann, H. A., Leaching tests at New Cornelia: Trans. Am. Inst. Min. Eng., vol. 55, 1916, p. 839.

[21] Smith, J. D. A., The Pechey leaching process: Chem. Eng. Min. Rev., vol. 14, 1922, pp. 177–181; Min. Mag., vol. 25, 1921, pp. 322–323.

[22] Greenawalt, W. E., Hydrometallurgy of copper. 1912, pt. 2, p. 207.

[23] Sleeman, H. R., Copper leaching at Whim Well, West Australia: Min. Mag., vol. 27, 1922, pp. 19–22.

[24] Irving, J., Heap leaching of low-grade copper ores: Eng. and Min. Jour., vol. 113, Apr. 29, 1922, pp. 714–721; May 6, 1922, pp. 774–777.

[25] Chen, T. S., The purification of solutions by means of limestone in hydrometallurgical treatment of copper ores. Thesis, University of California, 1921.

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3. Under like conditions the rate of oxidation and precipitation of ferrous iron is much slower in solutions that contain copper than with ferrous sulphate alone.

4. Ferric iron is completely precipitated by limestone in the presence of copper solutions.

5. The copper entrained in the ferric precipitates ranges from 0.8 per cent from hot solutions to 3 per cent from cold.

6. Iron precipitates more slowly with coarse limestone, but the precipitate is more difficult to filter when fine limestone is used, except when long-continued agitation follows.

SUMMARY OF PREVIOUS WORK

A study of previous work shows that in spite of some conflicting conclusions, the removal of iron and aluminum, and incidentally arsenic, antimony, bismuth, and tin, from copper sulphate solutions has been effected satisfactorily in a number of processes, with various requirements. Details are generally lacking on operating or optimum conditions, methods of controlling reactions, or the theoretical basis of procedures. The authors have attempted in the following pages to supply some of the missing data.

ORDER OF PRECIPITATION OF METALS ORDINARILY FOUND IN COPPER SULPHATE SOLUTIONS FROM THE LEACHING OF COPPER ORES.

Metals that occur commonly in copper sulphate solutions from the leaching of copper ores are iron, aluminum, zinc, nickel, cobalt, manganese, magnesium, the alkali metals, bismuth, arsenic, and antimony, in a variety of proportions and combinations. Soluble silica may also be present.

IRON

Hildebrand[26] gives the point at which ferrous iron precipitates as ferrous hydroxide as pH=9, or an alkaline solution. He calls attention to the difficulty of determining a similar point for ferric iron by use of the hydrogen electrode because of the effect of the ferric iron on the electrode, the ferric ion being reduced by the hydrogen.

A modification of his method, suggested by Dr. J. A. Wilson and used by F. L. Browne[27] permits the use of hydrogen electrode in presence of the ferric ion. Doctor Browne gives the point of precipitation of ferric iron, or rather of its complete hydrolysis, as lying between pH=2 and pH=3 (p. 307[27]). This agrees completely with results for the point of precipitation obtained by use of the air electrode in a large number of titrations in the Bureau of Mines laboratory, as will be noted in connection with the discussion of experimental results.

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[26] Hildebrand, J. H., Some applications of the hydrogen electrode in analysis, research, and leaching: Jour. Am. Chem. Soc., vol. 35, 1913, pp. 847–871.

[27] Browne, F. L., The constitution of ferric oxide hydrosol from measurements of the chlorine and hydrogen-ion activities: Jour. Am. Chem. Soc., vol. 45, 1923, pp. 297–311.

Jordis[28] showed that the point at which ferric iron was completely precipitated, as well as the related point at which it began to precipitate, depends first on the concentration of the ferric ion in the solution and second on the precipitant or hydrolytic agent used. His results show complete precipitation of ferric iron by amounts of hydrolytic agent ranging from as little as 84 per cent of the stoichiometric equivalent, with ferric sulphate and ammonia in dilute solutions, to as high as 102 per cent of the stoichiometric equivalent. with ammonium carbonate and ferric chloride solution. It would obviously be impossible to give a pH for precipitation of ferric iron any significance without giving the data as to the concentration of the ferric ion and the precipitant used. The effect of carbon dioxide in solution on the hydroxyl ion concentration could not be overlooked in an exact statement of the maximum insolubility point. The temperature should also be given, as the hydrolysis of ferric salts varies widely with the temperature.[29]

For technical purposes, Doctor Browne's[30] statement that ferric iron precipitates between pH=2 and pH=3 is accurate enough and could not be made more definite to suit special circumstances without an undue amount of detailed work because of the number of variables that affect solubility.

ALUMINUM

Because of its importance in the purification of water supplies on a large scale, conditions that control the solubility of aluminum compounds and the maximum insolubility of aluminum hydroxide have been investigated by many scientists. A detailed discussion of the more recent papers alone is far beyond the scope of the present investigation. Those interested in such details will find excellent résumés of recent work, and numerous references to other research bearing on the technical application of the data, in papers by Buswell and Edwards[31], and by Wolman and Hannan.[32] The solubility of aluminum salts and of amphoteric compounds in general is discussed theoretically by Massink,[33] Prins,[34] and van de Sande Bakhuysen,[35] and the mathematical treatment of the problem is developed.

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[28] Jordis, E., Über die Fällungen in Metallsalzlösungen durch Alkalihydroxyd- und Carbonatlösungen: Ztschr. Elektrochem., Bd. 18, 1912, pp. 553–562.

[29] Goodwin, H. M., Über die Hydrolyse des Eisenchlorids: Ztschr. phys. Chem., Bd. 21. 1896, pp. 1–15. The effect of temperature, of colloidal ferric hydrate, and of a magnetic field on the hydrolysis of ferric chloride: Phys. Rev., vol. 11, 1900, pp. 193–214.

[30] Browne, F. L., work cited, p. 307.

[31] Buswell, A. M., and Edwards, G. P., Some facts about residual alum in filtered water. Chem. and Met. Eng., vol. 26, 1922, pp. 826–829.

[32] Wolman, Abel, and Hannan, Frank, Residual aluminum compounds in water-filter effluents: Chem. and Met. Eng., vol. 24, 1921, pp. 728–734; vol. 25, 1921. p. 502.

For this paper it may be enough to note that different investigators have found that the point of maximum insolubility of aluminum hydrate varies from pH=6.5[36] to pH=8,[37] and that aluminum hydrate may be present as a solid over a range from pH=4 to pH=11. The solubility of the precipitate varies with the temperature, the dilution from which precipitated, the nature of the precipitant, and the presence in the solution of such impurities or accompanying substances as carbon dioxide or silica, as well as with the acidity of the solution. Another complicating feature both with aluminum and ferric iron precipitates is the fact that the first precipitate from sulphate solutions is not the hydroxide but a complex or a mixture which is sometimes a true basic sulphate of iron or aluminum and sometimes, notably at higher temperature, a mixture of the hydrate with basic sulphate. Posnjak and Merwin[38] determined the composition of a number of possible basic ferric sulphates. The only one met in this work is the most basic one they describe, of formula $3Fe_2O_3.4SO_3.9H_2O$.

Williamson[39] in like manner discusses basic aluminum sulphate.

The existence of colloidal ferric and aluminum hydrosols complicates the matter still further. Pauli and Matula[40] conclude, from a study of ferric oxide hydrosols, that "the sol appears as a complex salt, whose anions are identical with the anions of the ferric salt from which the sol was made," and that "the following formula would perhaps represent the sol—$x\ Fe(OH)_3.\ y\ Fe'''\ 3y\ Cl$.

Adolf and Pauli[41] reached similar conclusions as to the nature and composition of aluminum hydrosol. Tian[42] shows that the colloidal part of the solution reacts with the other phases present, and in so far complicates reactions where colloids are present in hydrolytic reactions.

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[33] Massink, A., De minimum-oplosbaarheid van aluminiumhydroxyde in water: Chem. Weekblad, Jahrg. 19, 1922, p. 66.

[34] Prins, A., De voorwaarden de maximum-praecipitatie van een amphoter electrolyt: Chem. Weekblad, Jahrg, 18, 1921, p. 657.

[35] van de Sande Bakhuysen, W. H., De waterstofionen-concentratie eener waterige oplossing van een amphoteer oxyd: Chem. Weekblad, Jahrg. 19, 1922, pp. 41–43.

[36] Blum, William, The determination of aluminum as oxide: Jour. Am. Chem. Soc., vol. 28, 1916, pp. 1282–1297.

[37] Smith, O. M., The coagulation of clay suspensions and silicic acid: Jour. Am. Chem. Soc., vol. 42, 1920, pp. 460–472.

[38] Posnjak, E., and Merwin, H. E., The system, Fe_2O_3-SO_3-H_2O: Jour. Am. Chem. Soc., vol. 44, 1922, pp. 1965–1994.

[39] Williamson, F. S., Basic aluminum sulphates: Jour. Phys. Chem., vol. 27, 1923, pp. 284–289.

[40] Pauli, von W., and Matula, Johann, Die physikalisch-chemische Analyse des Eisenoxydsols: Koll. Ztschr., Bd. 21, 1917, pp. 60–61.

[41] Adolf, von M., and Pauli, von W., Die physikalisch-chemische Analyse der Aluminumoxysalze und Aluminumoxydsole: Koll. Ztschr., Bd. 29, 1921, p. 281.

[42] Tian, A., L'hydrolyse lente des sels: Jour. de chim. phys., t. 19, 1921, pp. 190–216.

Ley[43] showed that the hydrolysis of aluminum salts increases noticeably with rise in temperature.

In technical application of the data in this report it may be of more practical value to know at what acidity and under what other conditions the greater part of the iron or aluminum is precipitated, because in passing from the pH at which the greater part of the iron or aluminum is precipitated to that at which the maximum insolubility exists there might be a loss of copper disproportionate to the small additional amount of iron or aluminum removed by so doing. As a practical solution of this highly complex problem—for technical purposes at least and with some refinements for accurate research—the authors suggest the titration of small samples of the solution to be purified with the hydrolytic agent to be used under the conditions of the run to be made, using the air electrode as an indicator to follow the course of the reaction. They have found that the course of voltage-acidity curves indicates satisfactorily when ferric iron is precipitated and when the bulk of the aluminum is precipitated, as well as the point of maximum insolubility, while certain idiosyncrasies of the curve indicate whether it is ferric iron or aluminum that is causing the particular change in the curve. Titration of a small portion in this manner gives a satisfactory guide for treatment of a large amount of the same solution, without the necessity for using the electrodes with the large volume of solution, once the ratio of hydrolytic agent is established by the small-scale experiment.

COPPER

The precipitate obtained from copper solutions on hydrolysis is a basic compound, which on boiling or long standing passes over into hydrated oxide. The nature of the basic compound first formed and its solubility depend on the hydrolytic agent used, the temperature, and the concentration of the copper and hydrolytic solutions. For example, Prescott and Johnson[44] claim that "Carbonates of fixed alkali metals—as potassium carbonate—precipitate the greenish-blue basic carbonate $Cu_2(OH)_2CO_3$ of variable composition, according to conditions, and are converted by boiling to the black, basic hydroxide $Cu_3O_2(OH)_2$ and finally to the black oxide. Barium carbonate precipitates completely, on boiling, a basic carbonate."

Free[45] studied the solubility of copper carbonates in water containing carbon dioxide. His study concerns the present investigation

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[43] Ley, H., Studien über die hydrolytische Dissociation der Salzlösungen: Ztschr. phys. Chem., Bd. 30, 1899, pp. 194–257.

[44] Prescott, A. B., and Johnson, O. C., Quantitative chemical analysis: A guide in quantitative work, with data for analytical operations and laboratory methods in inorganic chemistry. 5 ed., 1903, p. 106.

[45] Free, E. E., The solubility of precipitated basic copper carbonate in solutions of carbon dioxide: Jour. Am. Chem. Soc., vol. 30, 1908, pp. 1366–1370.

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because of the presence of carbon dioxide in most of the solutions used or because of the use of carbonates as hydrolytic agents. From Free's data it would appear that the carbonate obtained under the conditions of his experimental work formed at pH=6.9. He corroborates Prescott and Johnson[44] as to the variable composition of the copper precipitate obtained by different agents and under different conditions.

The authors find that on titration copper precipitates with alkali hydroxides at a point very close to neutrality when the air electrode is used as an indicator. In fact, it has been proposed to use the point at which deeply colored copper precipitate begins to form as the end point in the titration of complex metal solutions, to determine their " free " acid, using the appearance of the copper precipitate in lieu of the usual indicators whose color would be masked by the precipitates from ferric iron, aluminum, and other metals.

ZINC, NICKEL, COBALT, MANGANESE, SILICA, AND FERROUS IRON

These metals and the silica are treated, together, because they all precipitate at a higher alkalinity than does copper (as noted on p. 9, for ferrous iron). In practical work it is usual to remove the copper from the solution by cementation on iron, by electrolytic separation, or by selective hydrolysis, precipitating the copper without precipitating the nickel, cobalt, zinc, or manganese. The patents of Dow and Gates,[46] the thesis of Hickey and McIver,[47] and the paper of Hayward[48] on extraction of Cuban nickel ore describe the separation of copper and nickel by selective hydrolysis. Millberg[49] describes precipitation of copper by milk of lime, followed by selective precipitation of cobalt and nickel from the filtrate, leaving zinc in solution; he also describes a separation of copper from manganese by precipitation of the copper with milk of lime, leaving the manganese in solution. The separation of copper from these latter impurities by cementation or electrolysis is so well known that no extended investigation has been made on the subject by the Bureau of Mines. The authors have carefully noted the order in which they precipitate.

Smith[50] finds that silicic acid is best precipitated by calcium hydroxide at pH=9 and by aluminum hydroxide at pH=8 to 8.5.

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[46] Dow, H. H., and Gates, W. S., Process of separating metals in solution, U. S. Patents 913,708 and 913,709.

[47] Hickey, J. H., and McIver, R. W. E., The differential precipitation of metals from complex leach solutions. Thesis, Massachusetts Inst. Tech., 1922.

[48] Hayward, C. R., Extraction of nickel and alumina from Cuban ores: Chem. and Met. Eng., vol. 26, 1922, pp. 261–266.

[49] Millberg, Karl, Kupfer-vitriolgewinnung aus Kiesabbränden und minderwertigen Kupfererzen: Chem. Zeit., Jahrg. 30, 1906, pp. 511–513.

[50] Smith, O. M., The coagulation of clay suspensions and silicic acid: Jour. Am. Chem. Soc., vol. 42, 1920, pp. 460–472.

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Betterton[51] discusses in detail the effects and treatment of colloid silica in the related problem of purification of zinc sulphate solutions.

Because of the relative ease of separation of copper from zinc, manganese, cobalt, and nickel, a detailed study of these separations has not yet been made by the Bureau of Mines. Because of the difficulty of removing iron and aluminum from copper solutions, as well as the desirability of such removal in technical work, and because arsenic, antimony, and bismuth are usually removed completely during adequate removal of iron, first consideration has been given to the removal of iron and aluminum.

IRON AND ALUMINUM AS IMPURITIES IN COPPER SULPHATE SOLUTIONS

FERRIC IRON

Ferric iron is perhaps the most troublesome impurity in the hydrometallurgy of copper. In the electrodeposition of copper the presence of ferric iron in small proportions lowers the current efficiency seriously and, at slightly larger concentrations, prevents the deposition of any copper.

Addicks[52] determined the effect of various proportions of ferric iron on current efficiency in the electrodeposition of copper, finding decreases in efficiency ranging from 31 per cent with 0.06 per cent ferric iron, to 100 per cent with 0.75 per cent ferric iron at 123° F. He therefore emphasizes the necessity of "keeping liquors running more than some 0.2 per cent, and preferably much less, in ferric sulphate, away from intimate contact with the cathode, which means either a diaphragm or an efficient utilization of SO_2 or other reducing agent."

Middleton[53] tested the effect on current efficiency in copper electrodeposition of 0, 2, 4, 6, 8, 10, and 12 grams of ferric iron per liter, and found corresponding current efficiencies of 97, 92, 82, 68, 53, 37, and 27 per cent.

Larrison[54] and Greenawalt[55] explain the effect of ferric sulphate in retarding the deposition of copper by the reaction:

$$Cu+Fe_2(SO_4)_3=CuSO_4+2\ FeSO_4$$

"That is, copper already deposited or on the point of being deposited is attacked by the ferric sulphate and dissolved thereby, also reducing the ferric to ferrous sulphate." A small amount of ferric iron in solution, however, is desirable to prevent the formation of " brown " cathodes.

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[51] Betterton, J. O., Soluble silica in the preparation of zinc sulphate solutions for electrolysis: Trans. Am. Inst. Min. Eng., vol. 69, 1923, pp. 159–175.

[52] Addicks, Lawrence, The electrolysis of copper sulphate liquors using carbon anodes: Met. Chem. Eng., vol. 13, 1915, pp. 748–755.

[53] Middleton, P. C., Electrolytic deposition of copper in the leaching of roasted ore and concentrates: Min. and Sci. Press., vol. 119, 1919, pp. 149–151.

[54] Larrison, E. L., Influence of iron in copper electrolysis: Eng. and Min. Jour., vol. 84, 1907, pp. 442–443.

[55] Greenawalt, W. E., Hydrometallurgy of copper. 1912, pt. 2, p. 299.

Removal of iron to below 0.2 per cent, leaving the trace necessary for prevention of brown cathodes, would evidently be the desirable procedure; therefore this is the problem presented for solving.

In copper sulphate solutions from which copper is precipitated by cementation on iron, ferric iron causes waste of the scrap iron used for precipitation, dissolving half its weight of metallic iron in being reduced to the ferrous state. The ferric iron is controlled in practice by pyritic filters or SO_2, either of which reduces the ferric iron just before the leach solution is sent to cementation.

Irving[56] states, however, that in heap leaching, despite the use of pyritic filters, ferric iron often accumulates in the leaching solution until it causes a loss of scrap iron that seriously affects profitable operation of the process. Ferric iron also causes separation of insoluble basic salts of iron either in the heap, in heap leaching, or in vats or the other parts of the circulating system in vat leaching. At times this deposition necessitates shutting down operations in order to remove the mud of precipitated ferric compounds. Ferric iron in cementation processes also causes fouling of the copper precipitate as its percentage increases. Irving[56a] concludes that the control of ferric iron deserves thorough study. The same difficulties from ferric iron are present, but probably to a smaller extent, in the precipitation of copper from mine waters by cementation and in the electrolytic refining of copper.

ALUMINUM

The effects of aluminum as an impurity in copper sulphate solutions appear mainly in the electrodeposition of copper. Aluminum in amounts exceeding 4 per cent causes excessive foaming in electrolytic cells. Its presence markedly reduces the corrosion of copper cathodes by ferric iron, so that up to the trouble-causing limit its presence is desirable.[57]

In leaching, excess aluminum acts similarly to ferric iron in precipitating basic aluminum sulphate mud in the heaps or vats and the circulating system. The same hydrolytic treatment which removes ferric iron from solution removes aluminum, although to a smaller extent.

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[56] Irving, Joseph, Heap leaching of low-grade copper ores: Eng. and Min. Jour. Press., vol. 113, 1922, pp. 714–721.

[56a] Irving, Joseph, work cited, p. 719.

[57] Addicks, Lawrence, The electrolysis of copper sulphate liquors using carbon anodes: Met. and Chem. Eng., vol. 13, 1915, pp. 748–755; Process of recovering metals by electrolysis, U. S. Patent 1,138,921, May 11, 1915.

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FERROUS IRON

At times ferrous iron accumulates in cyclic processes until it causes trouble by crystallizing out the double sulphate of copper and ferrous iron, blocking pipes, and causing the loss of copper.[58]

The manufacturers of bluestone, however, have the most trouble with ferrous sulphate. On evaporation to obtain successive crops of copper sulphate, the ferrous sulphate present accumulates in the mother liquors until it begins to crystallize out with the copper sulphate, at a concentration of about 25 grams of ferrous iron per liter. This has been controlled either by sending the foul solution to cementation and precipitating out the copper, or by the Hofmann process, as noted on page 3.

In electrolytic processes, the presence of ferrous iron is advantageous in itself because of its effect as a depolarizer of the anode. Addicks[59] found that the presence of ferrous iron in amounts up to 1.5 per cent lowers the cell voltage by amounts up to 0.8 volt. This depolarizing is absolutely essential for carbon anodes. Addicks says "A carbon anode must be thoroughly depolarized or the liberated oxygen will attack the anode itself and the graphite will disintegrate, leaving a valueless sludge."

Since, however, the depolarizing effect of ferrous iron depends upon its oxidation to ferric iron at the anode, either the initial concentration of ferrous and total iron must be kept below the concentration at which ferric iron begins to be a serious menace to efficient operation of the cells, or some method of controlling ferric iron by reduction or by removal or separation from the cathode must be used.

HYDROLYTIC AGENTS

Numerous methods and reagents have been proposed for the purification of copper sulphate solutions—by precipitating out the copper with iron, sulphur dioxide under pressure, or hydrogen sulphide; by precipitating out impurities; or by rendering them harmless without removal. The authors have limited this investigation to the study of hydrolytic agents.

The greater part of the work has been done with hydrolytic agents that are most easily available for technical use because of cheapness or wide distribution. Certain otherwise desirable agents have not been used because they leave undesirable soluble salts in solution.

The three limitations of cost, availability, and suitability to the other conditions of the processes practically limit the hydrolytic agents to carbonates and oxides of copper and calcium. Calcium carbonate has been used as ground limestone and as dolomite, and calcium oxide as the ground solid and as milk of lime. Copper carbonate has been used in the form of various native ores, and copper oxide as obtained by calcining cement copper, copper sulphide ores, and concentrates.

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[58] Morse, H. W., and Tobelmann, H. A., Leaching tests at New Cornelia: Trans. Am. Inst. Min. Eng., vol. 55, 1916, p. 839.

[59] Addicks, Lawrence, work cited.

Any free acid present in practically all technical copper sulphate solutions must evidently be neutralized before any iron or aluminum can be precipitated by any of the above agents. Moreover, the sulphate radical combined with iron or aluminum must go to the copper or calcium added in the hydrolytic agent. If calcium compounds are used as hydrolytic agents, the sulphuric acid and the sulphate ion are lost to the process, in the form of insoluble and low-value calcium sulphate. When copper compounds are used for hydrolysis, all the sulphuric acid and the sulphate ion are saved; in fact, Du Faur points out that an undesirable excess of acid can be saved by using a copper hydrolytic agent exclusively.

On account of the slight alkalinity of copper carbonates and oxide as compared with the corresponding calcium compounds, the purification reaction is much slower with copper compounds under like conditions and gives a precipitate that often is more difficult to filter.

EXPERIMENTS WITH COPPER SULPHATE SOLUTIONS

TESTS WITH LIMESTONE

To check conclusions from the literature and from theoretical considerations and to gain familiarity with the appearance and behavior of solutions and precipitates, preliminary tests with 80-mesh limestone were made at room and at boiling temperatures. The limestone was first agitated with solutions of ferrous and ferric sulphates, copper sulphate, and aluminum sulphate, then with combinations of two and three of these solutions at a time, and last with all four together.

As the authors expected, these experiments showed that most of the aluminum and ferric iron could be precipitated without much loss of copper, but that ferrous iron could not be precipitated as such without precipitating all the copper. All the ferric iron could be precipitated with only a small loss of aluminum in the precipitate, but practically all the aluminum precipitated out before ferrous iron began to precipitate. Copper precipitated completely from a solution of such acidity that it was acid to phenolphthalein and alkaline to methyl orange.

The tests showed that for selective precipitation of iron and aluminum that would leave copper in solution, ferrous iron must be oxidized to ferric either before or during the reaction. Since these solutions are acid in practice, and ferrous iron is known to oxidize much more slowly in acid than in neutral or alkaline solutions, it appeared best to carry on the oxidation of ferrous iron by blowing air through the solution during and after the addition of limestone, with or without additional mechanical agitation. Hanley[60] showed that in purifying zinc sulphate electrolyte solutions in a similar manner the oxidation of ferrous iron was much more rapid when the air bubbles were finely divided. Therefore, after the first of our quantitative runs, the air used for oxidation and agitation was blown into the lower part of the solution through canvas, filtros plates, the bottom of a Gooch crucible, or the arms of a rotary aerator stirrer to break up the bubbles as much as possible.

Most of the work was done with a standard solution containing, per liter, 30 grams of copper, 5 grams each of ferric and ferrous iron, and 10 grams of aluminum, all in the form of sulphates, with 15 grams of H_2SO_4 per liter to prevent hydrolysis.

The limestone used contained 97.98 per cent of calcium carbonate. The effect of the 1.3 per cent of magnesium carbonate impurity in the limestone was determined by agitating known mixtures of magnesium carbonate and calcium carbonate, of magnesium sulphate and calcium carbonate, and of magnesium carbonate and calcium sulphate, with solutions of aluminum sulphate, ferric sulphate, and copper sulphate. Results showed that the magnesium carbonate had no effect on the iron, aluminum, or copper in the presence of the calcium carbonate; and it did not affect any constituents of the complex copper-iron-aluminum-acid solution even after several days' agitation with minus 200-mesh magnesium carbonate as magnesite alone. At room temperatures magnesium carbonate may be considered an inert substance so far as this reaction is concerned.

AMOUNT OF LIMESTONE NEEDED

The amount of limestone needed to precipitate the iron and aluminum and leave the copper in solution could be determined only by trial, because the alkali or alkaline earth hydrates or carbonates needed to precipitate iron or aluminum completely from their sulphate or chloride solutions is rarely 100 per cent of the stoichiometric equivalent, and in most solutions falls from 5 to 25 per cent below that amount.[61] The amount necessary under given circumstances can only be determined by "bracket" runs with too little and too much limestone, converging to the optimum, on small samples of the solution, or by use of the electrometer as indicated on page 12.

Experiments were begun, therefore, with 100 per cent of the stoichiometric equivalent of limestone to precipitate the total iron and aluminum and neutralize the added sulphuric acid in the solution of composition noted above. A solution of this composition was chosen as the general average of a number of commercial solutions. Variations in each constituent were made in special runs, to determine the effect of the excess and absence of each constituent.

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[60] Hanley, H. R., Electrolytic zinc methods: Min. and Sci. Press, vol. 121, 1920, pp. 795–804.

[28] Jordis, E., Über die Fällungen in Metallsalzlösungen durch Alkalihydroxyd- und Carbonatlösungen: Ztschr. Electrochem., Bd. 18, 1912, pp. 553–562.

The limestone-solution pulp was aerated in a 3-liter glass cylinder with a bottom of filtros plate cemented in place with Khotinsky cement. Air came up through the filtros bottom finely divided.

The first runs were blown 60 minutes only and introduced an unexpected complication. When the pulp was filtered, the iron and aluminum passed into the filtrate as colloids, deep brown in solution, leaving clear, white calcium sulphate on the filter. The solutions were very stable; one has remained in the laboratory without apparent change for a year.

The trial runs indicated that purification of copper sulphate solutions on a practical basis was impossible until the handling of these colloidal solutions was understood. Indeed, many earlier investigators have given up the purification of copper sulphate solutions by hydrolytic agents as hopeless, because the amount of copper precipitated was prohibitively great when the hydrolytic agent was used strong enough to give noncolloidal solutions; and they made no attempt to break up the colloidal solutions obtained when enough hydrolytic agent was used to precipitate iron and aluminum, after flocculation, without loss of copper.

Therefore, a series of runs was made, using 100 per cent of the theoretical equivalent of limestone to precipitate total iron and aluminum, putting aside for the moment the question of the best proportion of limestone, in order to study the colloid solutions. The numerical results are recorded in Table 1 following, with fuller explanation in text following.

TABLE 1.—*Runs made with 100 per cent of the theoretical equivalent of limestone to precipitate total iron and aluminum*

[Copper sulphate solution as noted (p. 17), except where otherwise stated; 100 per cent equivalent of noncopper components of solution used, as 80-mesh limestone; aeration in 3-liter glass cylinder, through filtros bottom, first seven runs, and in filtros-bottom 200-c. c. glass cylinder, last four; all at room temperature.]

Run No.	Time of aeration	Results.
1	60 minutes	Filtrate colloidal Al and Fe''', filter cake clear white.
2	do	Same results. Quantitative change of $CaCO_3$ to $CaSO_4$ found.
3	do	Al left out of original solution. No colloid obtained.
4	do	Cu left out of original solution. Colloid obtained as in 1 and 2.
5	do	Check on run 3. Only trace of colloid found in filtrate, as shown by boiling test.
6	do	Cu and Fe''' omitted from original solution. No change in solution in 1 hour, but colloidal aluminum was shown by boiling filtrate after 1 more hour aeration.
7	60 minutes, total.	Al and Fe''' used alone and aerated 1 minute. Deep-brown colloid filtrate obtained. Solution replaced and aerated 60 minutes. Colloid still, but of lighter color, indicating breaking up of colloid first obtained.
8	5 minutes	Al alone, not aerated, but stirred with limestone and filtered after 5 minutes. Filtrate colloid, giving precipitate on heating, determined by analyses to be basic aluminum sulphate.
9	do	Fe''' alone, not aerated, but stirred with limestone and filtered after 5 minutes. Filtrate colloidal; filter cake clear white.
10	23 hours	To determine if long aeration would break up the colloid. Clear blue filtrate obtained, free from Fe or Al, brown filter cake.
12	7½ hours	To see if colloids would break up in shorter time. Filtrate colloid, and cake white at first, but colloid broken up by repeated filtration, leaving brown precipitate of iron on original white cake.
13	4½ hours	To try effect of further shortening time of agitation. Filtrate colloid, not broken up by repeated filtration, cake white.

The above data indicate that the colloid is due mainly to the presance of aluminum in the solution; at least its persistence is due to Al, as shown by omitting Al in runs 3 and 6 and getting only a trace of colloid. Run 4 shows that the Cu has no effect upon colloid formation, and run 6 that ferrous iron has no such effect. Run 9 shows that it is possible to get the colloid ferric solution alone, and run 8 that the colloid is formed instantly when the solution neutralizes and is not developed slowly as the reaction proceeds. Run 2 removes the suspicion that the limestone might not have reacted fully. Runs 10, 11 (see Table 3), and 12 show the time of agitation at room temperature necessary to break up the colloid by aeration combined with filtration.

BREAKING UP COLLOID SOLUTIONS

Experiments on breaking up colloid solutions by dilution and by boiling showed that the precipitation of iron and aluminum from the solutions was far from complete, while flocculation and precipitation by aeration was complete. In later work either the long-time aeration of 24 hours or the shorter aeration of 6 to 7 hours was used, with repeated filtration to break up the colloid filtrates. The effect of filtration in breaking up a partly flocculated colloid may be due to intense local agitation during filtration or to the effect of local pH change during filtration.[62] In the writer's experiments these colloid solutions were found only in work at room temperatures. They appeared in none of the filtrates from solutions purified above 40° C.

Such colloid solutions of iron and aluminum oxide hydrosols are frequently encountered by sanitary engineers in water-purification work. Flocculation is brought about in solutions of the dilution of ordinary water supply by filtration under pressure,[63] by control of pH by added milk of lime,[64] or by allowing the water to stand in storage reservoirs after oxidation of ferrous to ferric iron.

APPARATUS

During the earlier part of the investigation the authors had not yet perfected the type of apparatus that would permit heating the solutions and holding them at a definite high temperature; was large enough to allow sampling during runs without perceptible effect on the results as each sample was removed; was designed to permit mechanical agitation and fine-bubble aeration with measured amounts of air over periods of several days without interruption day or night and to permit control of evaporation losses; or was made of material resistant to the highly corrosive solutions and rapid changes of temperature in starting up and stopping runs. While the writers were trying out one design after another to fulfill these rather exacting requirements, the earlier runs were made at room temperature in apparatus that met the requirements at lower temperatures more or less satisfactorily.

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[62] Wolman, Abel, and Hannan, Frank, Residual aluminum compounds in water-filter effluents: Chem. and Met. Eng., vol. 24, 1921, pp. 728–734.

[63] Terhearst, von R., Das neue Gaswerk der Stadt Nürnberg: Jour. Gasbel., Jahrg. 47, 1904, p. 1106.

[64] Buswell, A. M., and Edwards, G. P., Some facts about residual alum in filtered water: Chem. and Met. Eng., vol. 26, 1922, pp. 826–829.

In the runs on colloid solutions ferrous iron had not oxidized as rapidly as had been hoped. Theoretical considerations and the first work made it plain that ferrous iron must be oxidized to ferric before it could be precipitated from a solution containing copper without the copper itself being precipitated by the hydrolytic agent. Aeration at room temperature during the first runs did not oxidize the ferrous iron completely in 24 hours.

Two methods were tried, with the hope of increasing the rate of oxidation of ferrous iron: The first used manganese dioxide; the second, a spray tower, as commonly employed for aeration or cooling of water.

OXIDATION OF FERROUS IRON WITH MANGANESE DIOXIDE

The numerical results of the runs with manganese dioxide are summarized in Table 2 following, with further explanation in the text.

TABLE 2.—*Oxidation of ferrous iron in copper sulphate solutions by* MnO_2

Run No.	MnO_2	Mesh	Treatment	Results
	Amount added			
	Grams			
14	[a] 0.47	....	Shaking, cold	Immediate solution of MnO_2 and oxidation of equivalent of Fe''.
15	0.47	−180	Boiling 2 hours	Solution of all MnO_2 and oxidation of equivalent of Fe''.
16	20	−180	Aeration 6½ hours	0.11 g/l Fe'' left (5 g/l original).
17	15	−180	Aeration 6 hours	0.1 g/l Fe'' left.
18	12.63	−180	Aeration 3¼ hours	Do.
19	10	−180	Aeration 1¼ hours	Do.
20	10	−180	Aeration 40 minutes	Do.
21	17.8	−180	Aeration 35 minutes	0.1 g/l Fe'' left; 0.1549 gram MnO_2 dissolved instead of theoretical 0.4663 gram necessary for oxidation of total Fe''.
23	10	−100	Aeration 1 hour 35 minutes.	Only trace Fe'' remaining; 0.0767 gram MnO_2 found on analysis of solution, instead of 0.6526 gram necessary if MnO_2 did all the oxidation, or 12 per cent of theoretical equivalent of manganese.

[a] Colloid.

When experiments with manganese dioxide were begun it was thought that it would act slowly if at all with the solutions used, because in the Weldon process for making chlorine "hydrochloric acid acts on the manganese dioxide until its concentration is reduced to about 5 per cent actual hydrochloric acid. With recovered manganese the acid is utilized down to about 2 per cent."[65] The first manganese dioxide used was made as the colloid by precipitation from potassium permanganate solution with ammonia, in order that it might be as finely divided as possible, because the acidity of the solution was originally but 1.5 per cent. It immediately dissolved in the solution cold. The next runs show how ordinary manganese dioxide, as powdered pyrolusite, reacted with the ferrous iron in the solutions. First the solution was boiled, and when the manganese dioxide dissolved with quantitative oxidizing effect large amounts were tried with cold solutions for a long time; the time was then shortened and the amount of manganese dioxide used reduced. It was suspected that the action might be catalysis, hence the final solution was analyzed for manganese as well as for ferrous iron in the last two runs. In the last run 12 per cent only of the theoretical equivalent of manganese dissolved; meanwhile the ferrous iron had oxidized in less than 7 per cent of the time necessary for the same amount of oxidation without the manganese dioxide. This shows conclusively that the manganese dioxide catalyzes the oxidation by aeration to a marked degree.

Du Faur[66] successfully used 43 per cent of the theoretical amount of manganese dioxide for oxidation of ferrous iron in similar copper sulphate solutions and obtained a 92 per cent oxidation in 2½ hours aeration. He advises adding the manganese dioxide by parts during the oxidation, because less sulphate ion is lost during the precipitation of basic ferric sulphate if the dioxide is added thus.

The writers found that most of the dissolved manganese was precipitated later when the oxidized iron and the aluminum were precipitated by means of limestone from the solution which had been treated with manganese dioxide. In one trial, 0.0186 gram per liter of Mn (run 34) was left in the finally treated solution; and in a second, 0.012 gram per liter of Mn (run 40).

A small amount of manganese in solution would present no difficulty in electrodeposition of copper from the solution, because it would deposit on the anode as hydrated manganese dioxide, and in time would drop off as recoverable sludge. If the manganese were allowed to accumulate in bluestone manufacture it would have to be removed in time, but the thoroughness of removal during precipitation runs shows that it could be done satisfactorily when necessary.

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[65] Rogers, Allen, and Aubert, A. B., Industrial chemistry, a manual for the student and manufacturer. 1912, p. 237.

[66] Du Faur, B., Hydrometallurgical research: Chem. Eng. Min., Rev., vol. 12, 1920, p. 243.

ELECTROMETRIC CONTROL OF REACTIONS IN PURIFICATION

As the sampling of solutions during aeration was difficult and changes in volume due to evaporation were hard to control, a platinum electrode of platinized foil about 1 cm. square and the salt bridge of a normal calomel electrode were introduced into the solution in run 20, to see if the course of the oxidation could be followed by the changes in the ferro-ferri potential, as shown by the measured electromotive force of the cell so set up. The potential was measured by the well-known Poggendorff compensation method, against a storage battery and Weston cell by the usual bridge method.

The form of curve obtained in this and later oxidation runs is illustrated by the graphs in Figure 1.

At the flat part of the curve the ferrous iron was found to be oxidized to a very small residual amount (see analyses in the tables). A complete oxidation shows an additional sharp rise in the curve toward the end.

For proof that the curve was due to the oxidation of ferrous iron, more ferrous sulphate was added after run 22 was completed and the voltage fell instantly, then began to rise again as before. Manganese sulphate added to the solution had no effect either on the course of the oxidation or the voltage-time curve.

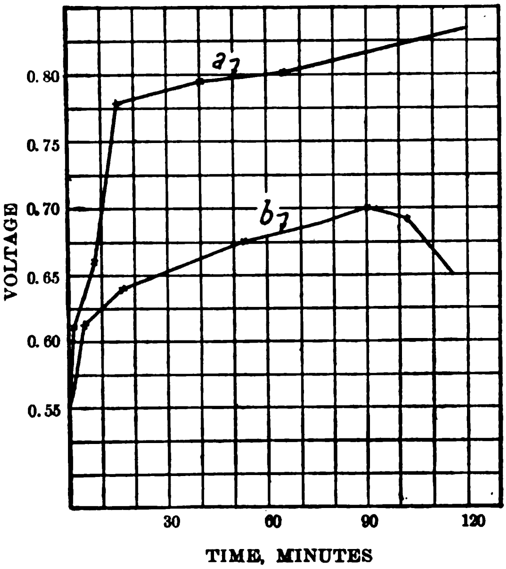

FIGURE 1.—Oxidation of ferrous iron by manganese dioxide and air. Graphs (voltage-time curves) of electromotive force of a platinum (air) electrode versus a normal calomel electrode in the solution being oxidized: *a*, Oxidation of a discarded leaching solution from the Mountain Copper Co., containing 0.19 gram of Cu, 13.8 grams of FeO, no Fe_2O_3, 5.2 grams of Zn, and 2.45 grams free H_2SO_4 per liter; *b*, oxidation of ferrous iron in solution from decomposition of ferruginous clay by H_2SO_4, using MnO_2 and air.

LIMESTONE AND COPPER OXIDE AS HYDROLYTIC AGENTS

Since the Pt-HgCl cell followed oxidation by manganese dioxide, it was tried in the following series in order that the oxidation of ferrous iron might also be measured in those runs where ferric iron and aluminum were precipitated by some hydrolytic agent and the ferrous iron oxidized by aeration. In practically every run a graph was obtained like one of those shown in Figure 2. Since electrodes had been used in measuring oxidation by the ferro-ferri potential change, it was natural that the curves should be interpreted in terms of oxidation of iron. Later work proved this erroneous. The drop in the first part of the curve is due to neutralization of the free and hydrolytic acid in the solution, and the rise in the second part is due mainly to the setting free of acid by hydrolysis of basic ferric and aluminic sulphates which form at the moment of neutralization and are later hydrolyzed by the solution—cold solutions slowly and hot rapidly.

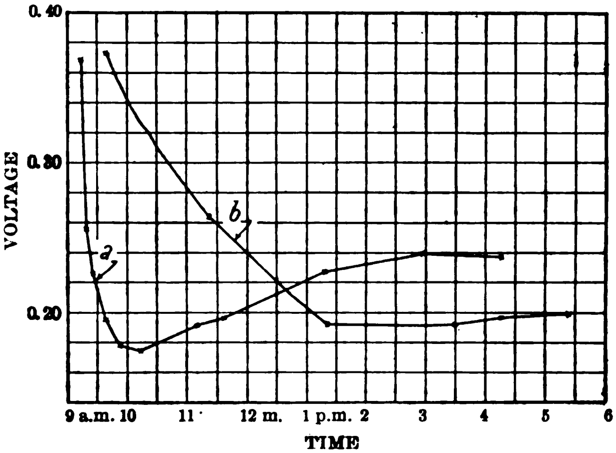

FIGURE 2.—Voltage-time graph, during purification of impure copper solutions: *a*, Limestone as hydrolytic agent; *b*, copper oxide as hydrolytic agent. The curves show the initial drop in voltage on neutralization with air versus calomel electrode, and the slow rise that followed. Both fall and rise are slower with copper oxide than with limestone.

DIFFERENT USES OF ELECTRODES

The fact that one electrode may be used at one time in the same or similar solutions to determine oxidation and reduction conditions, and at another to indicate acidity and alkalinity relations may possibly need further explanation. The theoretical basis for this double function of the oxygen electrode may be found in discussions by Fredenhagen[67] and by Crotogino.[68]

Fredenhagen shows from theoretical considerations that the alkali-acid ratio should not affect the ferro-ferri potential, although in practice variations from the theory are found at high concentrations. Crotogino develops the converse proposition that the ferro-ferri ratio should not and does not under ordinary conditions affect the potential due to the acid-alkali ratio. He gives approximate curves showing pOH—voltage for different acid concentrations, with the platinum-oxygen electrode versus the calomel electrode. Figure 3 is such a curve.

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[67] Fredenhagen, Carl, Zur Theorie der Oxydations und Reduktionsketten: Ztschr. anorg. Chem., Bd. 29, 1902, pp. 396–458.

[68] Crotogino, F., Studen über Oxydationspotentials: Ztschr. anorg. Chem., Bd. 24, 1900, pp. 225–262.

A study of these two factors shows that if the oxidation condition is not changed during the reaction the oxygen electrode will indicate, by its voltage changes, conditions during neutralization of the acid by alkali and the reverse; or, if the acid-alkali ratio is not changed during the reaction, will show oxidation-reduction changes just as plainly. If both change simultaneously in the same reaction medium, the electrode changes would be very difficult if not impossible to interpret.

When aluminum was precipitated by limestone as basic sulphate from an iron-free aluminum sulphate solution, the voltage-time curve fell sharply at first and rose more slowly, as is typical when iron is present in solutions. Curves for zinc and copper similarly precipitated dropped and rose to a smaller degree, so that the sudden drop and slow rise are characteristic of something other than the ferro-ferri change. After the solution was actually analyzed for acidity and the rise in voltage found to correspond to the rise in acidity, and after pure basic ferric sulphate was agitated in water and the acidity of the water was found to rise slowly in the cold and rapidly in the hot, it was determined that this slow rise was due to the development of free acid from the hydrolysis of basic sulphates in the solution. When the basic sulphate was analyzed after it had been filtered out from suspension in water and dried, it had been changed into ferric oxide of an amount equivalent to the acid set free in the water while it was decomposing during agitation.

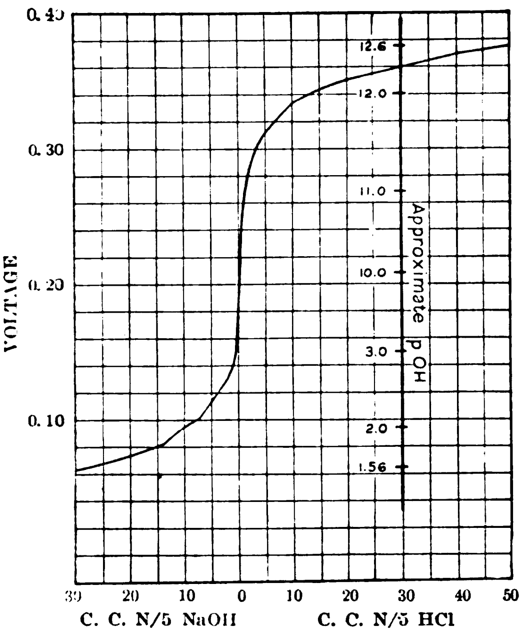

FIGURE 3.—Voltage-concentration changes, during neutralization of acid by alkali, with an air electrode versus a normal calomel electrode indicator

The ferro-ferri potential undoubtedly appears to a certain extent in the slow rise of the second part of the curve of the potential, but the rate of oxidation is much slower than when MnO_2 is used, requiring hours as compared with minutes, and for the greater part of the run corresponds to the flat part of curve *b*, Figure 1 (see p. 23) with manganese dioxide; hence the change in voltage due to ferro-ferri changes is entirely overshadowed by the change due to acidity increase.

DETERMINATION OF OXIDATION OF FERROUS IRON

From the voltage of the oxygen (or, better, air electrode) therefore it is impossible to tell when the oxidation of ferrous iron in a copper sulphate solution undergoing purification is complete. This can be determined easily, however, by titration of a filtered sample with potassium permanganate. We can, however, determine a thing very much more difficult to estimate, and of just as much importance in the control of the reaction, namely, the alkalinity of the reaction mixture.

In a solution containing ferric iron, aluminum, and much copper the determination of acidity by titration with the ordinary indicators is at best very difficult and doubtful, and the use of colorimetric standards is excluded on account of the deeply colored solution or precipitates. With the electrodes as described, the large and characteristic voltage changes indicate the neutral point perfectly when the solution is titrated with standard alkali. Furthermore, in titrating a solution containing ferric iron there is always a typical "knick" (bend) in the curve of voltage versus added alkali as the ferric iron precipitates, giving a characteristic long gradual slope ending in a sharp drop, as most of the aluminum precipitates before the neutral point at which copper precipitates.

The use of this fact in controlling the removal of ferric iron and aluminum from copper solutions by the addition of limestone or other hydrolytic agent is at once evident. It is impossible to calculate the amount of hydrolytic agent necessary to cause the precipitation, for reasons stated above (p. 10). However, by using the electrodes and adding the hydrolytic agent cautiously it is possible to tell by the characteristic "knick" in the voltage curve just when the ferric iron begins to precipitate and, by the following flat part of the curve, when most of the aluminum is precipitated; then, during the course of the reaction later, hydrolytic acid can be reduced, as it develops, to the point where ferrous iron is easily oxidized by aeration with the addition of small amounts of the hydrolytic agent controlled by the drop in the potential of the electrodes. At the end of the reaction the acidity at which any precipitated copper redissolves can be maintained by adding a little acid, as controlled by the same electrode, without redissolution of the precipitated ferric iron and aluminum.

USE OF PLATINUM-NORMAL ELECTRODE CELL

As was found on trial with large-scale runs, it is possible, but extremely difficult and doubtful, to control the reaction in the same way by determinations of free acid in filtered samples, using a methyl orange indicator, for example, and titrating against standard alkali, diluting the samples considerably. There are satisfactory methods for determining free acid in complex mixtures of metals, but for laboratory control of commercial processes they are all far too slow. The authors have therefore used the platinum-normal electrode cell as an indicator throughout the investigation of these purification reactions. Typical curves are shown in Figure 4, with curves of neutralization of ferrous, ferric, and aluminum solutions by alkali.

For the control of large-scale operations, the electrode can be obtained in the commercial form made by Leeds-Northrup, whose research has shown that the electrode, originally designed as a hydrogen electrode, works just as well when used as an air electrode.[69] The use of the electrode in control of large-scale operations is described in the same article.

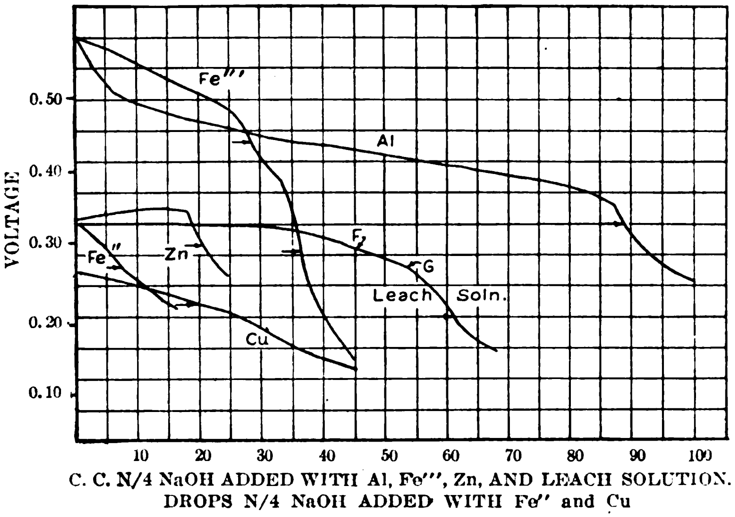

FIGURE 4.—Types of graphs, showing voltage-concentration changes on neutralization. The "knick" at the upper arrow in the Fe''' curve is characteristic of ferric iron. It appears again at point F in the curve for the leach solution, showing that the ferric iron present has been precipitated, although the solution is still acid. The point G on the curve for leach solution shows the precipitation of aluminum. The lower arrows on each curve indicate the point of neutrality, as defined by the maximum voltage change for added alkali. The forms of the curves are typical of the metals named with the graphs for the air-normal calomel electrode

The calomel electrode can also be kept out of the tank and the salt bridge and wire to the platinum electrode extended down into the tank inside a lead tube which is perforated at the lower end, and the wires from the electrodes can be led to the galvanometer outfit at any convenient place at any reasonable distance. It is, however, about as easy to take samples out of the tank and test them with a laboratory electrometer, because the reactions in the tank are much slower, or rather the lag after the reagent is added is so great that there is plenty of time to make any needed tests on removed samples without having the electrodes in the tank itself.

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[69] Arthur, R. C., and Keeler, E. A., A meter for recovering alkalinity of boiler-feed water: Power, vol. 55, 1922, p. 768.

In practice it is a good plan to run a small test sample of the solution to be purified, using reagents and temperatures as they will be with the large lot, in order to obtain the data on amounts, times, and so on. It is also advisable to follow the acidity of the solution during the run, as the oxidation does not begin until acidity is less than 1 per cent, and, when the run is completed, to determine the amount of acid to add to the precipitate to clean out entrained copper.

OXIDATION RUNS WITH SPRAY TOWER

Having shown in the runs of Table 2 that ferrous iron in impure copper sulphate solutions could be satisfactorily oxidized by the use of manganese dioxide, either with hot or cold solutions, the authors investigated next the oxidation of ferrous iron in the copper sulphate solutions by means of a spray tower; using the electrode arrangement described on page 23 in order to follow as closely as possible the course of the reaction, as in the work with manganese dioxide.

FIRST APPARATUS

The investigations of Schmidt and Bunte[70] and of Oesten[71] showed that falling drops of water absorb oxygen rapidly. Accordingly, the authors tried treating the impure copper sulphate solution, of previously stated composition, with the stoichiometric equivalent of limestone (—80-mesh) to precipitate total iron and aluminum and neutralize free acid, then circulating the mixture through a system composed of air lift, baffle plate, and falling-spray tower with air flowing counter-current to the mixture, a sump where the platinum electrode and salt bridge from normal electrode were immersed in the mixture flowing past, and glass-tubing connections. The arrangement permitted sampling just ahead of the baffle plate during the run. It was found that the oxidation in this apparatus was no more rapid than in the previously used glass cylinders with air blown up through a filtros or alundum bottom. Evidently the rate of absorption of oxygen from the air is not the limiting factor in the oxidation of ferrous iron, so far as these two methods of supplying air are concerned. This was shown for very dilute ferrous solutions by Schmidt and Bunte.[72]

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[70] Schmidt, A., and Bunte, K., Über die Vorgänge bei der Enteisenung des Wassers: Jour. Gasbel., Jahrg. 46, 1903, p. 481.

[71] Oesten, von G., Sauerstoffauf nahme des Wassers im Regenfall einer Enteisenungsanlage: Jour. Gasbel., Jahrg. 45, 1902, p. 283.

[72] Schmidt, A., and Bunte, K., work cited.

RESULTS

In the two runs with the spray tower it was found that 11 hours aeration reduced the ferrous iron by 25 per cent only (run 27), and that 27 hours aeration was necessary to oxidize ferrous iron completely in this way (run 26). During these two runs it was observed that a greenish precipitate of copper carbonate, due to local concentration of limestone, formed wherever the circulation in the tubes was slow enough for the reaction solids to settle to any extent. This conclusion as to the effect of allowing the reaction mixture to settle has been confirmed repeatedly.

CHANGES IN APPARATUS

As glass cylinders with porous bottoms were more convenient to operate than the spray tower, and apparently worked as well, the next tests were carried on in the cylinders, the air being blown through bottoms of filtros plate, alundum plate, or canvas. A series of runs was made with limestone to determine: 1, The best fraction of the stoichiometric equivalent of limestone to use to precipitate iron and aluminum without loss of copper; 2, the effect of changing the grain size of limestone used on the course of the reaction; 3, the effect of excess added ferrous iron, excess ferric iron, and excess aluminum; and 4, the probable effect of heating the reaction mixture, preparatory to the design of apparatus suitable for careful work at higher temperatures.

RESULTS

The numerical results follow in Table 3 with additional explanations in the text.

TABLE 3.—*Precipitation runs with limestone and impure copper solutions* [a]

Run No.	Limestone used	Precipitated—				Time of aeration	Notes
		Fe'''	Fe''	Al	Cu		
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*		
11	100	100	88	95.4	12.9	23 hours	
25	100	100	96	98	18.3	29 hours	
27	100	100	25	29.4	4.8	11 hours	Spray tower run.
28	93	100	100	97.7	34.5	24 hours	
29	84.6	93.1	total Fe	86.7	1.6	7 hours	
33	74.4	--------	--------	--------	--------	7 hours	So much Fe'' and Fe''' in filtrate by qualitative test that quantitative test was not made.
35	74.4	100	84.1	43.4	0.70	23 hours	Limestone added all at once.
36	74.4	100	83.7	84.5	.66	24 hours	Limestone added in portions gradually.
37	51.8	87.7	61	84.3	.4	23 hours	Effect of excess aluminum.
38	86.0	94.7	84.9	93	19.3	22 hours	Effect of excess ferrous iron.
39	85.2	99.5	90.8	99.8	20.8	23 hours	Effect of excess ferric iron.
51	96.8	71.8	35.2	8	.5	21 hours	Effect of using 20 to 40 mesh limestone.
54	98.2	95.8	35.6	n. d.	9.4	14 hours	Effect of using 20 to 40 mesh limestone, short run.
50	78.2	100	98	--------	20	38 minutes	Small-scale run at 75°, pilot run.
55	98.0	100	97.6	n. d.	.8	12½ hours	20 to 40 mesh limestone at 80° C.
61	78.2	94.3	69.0	89.1	3.42	5 hours	Run at 80° C. with −100-mesh limestone.
62	100	100	97.9	97.5	26.8	9 hours	Do.
63	78.2	74.3	52.4	81.5	4.4	7 hours	Check on run 61 at 20° C
64	78.2	88.1	88.9	81.1	8.2	15 hours	Like 63—longer run.
65	75.4	100	93.9	73.6	7.1	33½ hours	To get limit effect of small proportion of limestone aerated for a long time.

[a] −80-mesh limestone is used except when otherwise stated.

1. Table 3 shows that 100 per cent of the stoichiometric equivalent of limestone necessary to form ferric and aluminum hydrate causes a loss in the precipitate of amounts of copper ranging from 4.8 per cent (run 27) to 26.8 per cent (run 62), depending on time of aeration and on temperature.
2. At room temperature the amount of limestone causing least loss of copper in the precipitate (0.7 per cent) with reasonable removal of iron and aluminum is about 74.4 per cent of the stoichiometric amount (runs 35 and 36).
3. The effect of excess ferrous or ferric iron is to bring down a much larger proportion of copper in the precipitate, even though the limestone used is below 100 per cent.
4. The effect of excess aluminum is to reduce the amount of copper entrained in the precipitate to a very low figure (run 37).
5. Heating the reaction mixture reduces the time of oxidation of ferrous iron appreciably and lowers the proportion of limestone necessary for precipitation (runs 61 and 62).
6. Coarser limestone causes the reaction to go more slowly. Copper tended to precipitate on the surface of the larger grains, unless the agitation was very rapid (runs 51, 54, and 55).
7. Ferric and ferrous iron and aluminum can be removed from impure sulphate solutions without prohibitive loss of copper in the precipitate if the proper proportion of limestone is used, and if the reaction mixture is kept from settling in slowly moving spots (runs 35 and 36).

TESTS WITH OTHER HYDROLYTIC AGENTS THAN LIMESTONE

A number of other hydrolytic agents were tried, including calcium oxide, dolomite, magnesite, calcined copper sulphide ore (both high and low grade), azurite, malachite, cuprite, chrysocolla, and copper oxide (both chemically pure and made by calcining "cement" copper). The runs were made in the glass cylinder with a porous bottom through which the solution, except where otherwise stated, was aerated at room temperature, as with the preceding limestone runs. The numerical results are summarized in Table 4 following, with further explanation in the text.

TABLE 4.—*Hydrolytic agents other than limestone, with impure copper sulphate solutions*

Run No.	Hydrolytic agent	Time of aeration	Temperature	Amount precipitated				Notes
				Fe'''	Fe''	Al	Cu	
		Hours	° *C.*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
14	Lime, 100 per cent.	6	20	100	90.5	92.6	6.2	Very slow filtering precipitate.
45	Dolomite, 186 per cent.	23	20	100	46.1	13.4	0.98	Minus 200-mesh dolomite, with about 93 per cent of enough limestone by itself to precipitate Fe, etc.
52	Magnesite	12½	20	3.2	0	0	0	Minus 200-mesh magnesite used.
46	CuO, 100 per cent.	13½	20	91.0	48.9	8.4	N. d.	Fe'' partly preoxidized by MnO_2.
48	CuO, 350 per cent.	13	20	84.3	38.8	4.9	N. d.	
47	Calcined low-grade Cu ore.	12	20	19.3	8.2	17.8	N. d.	Ore calcined at 800°. Excess used.
53	do	18	80	51.0	23.7	N. d.	N. d.	Ore calcined at 800°. Half of above used.
49	do	10	20	All impurities increase.				Ore calcined at 600°. Excess used.
120	Azurite, 104 per cent.	25	20	79.7	39.6	16.3	85 gain	Very slow filtering precipitate.
127	Azurite, 41 per cent.	25	20	81.7	16.3	0	89.8 gain	Precipitate filtered with extreme difficulty; unchanged azurite in both runs, in final precipitate.
135	Cuprite. 51 per cent of theory.	5	20	All Fe to Fe''.		14 gain	41 gain	Metallic Cu in precipitate.
136	Chrysocolla, 40 per cent.	8	20	29.8	0	0	15.7 gain	Much unchanged chrysocolla.
138	Malachite, 37.7 per cent.	24	20	66.5	36.5	17.9	51 gain	Much unchanged malachite. Very slow filtering precipitate.
143	do	11½	20	Impossible to filter.				Not settled after 4 months.
140	Calcined Cu ore, Tucson, 20 per cent.	6	20	17.4	1.9	16.1 gain	4.5 gain	Filtered well.

EFFECT OF HYDROLYTIC AGENTS

LIME

Lime gives results similar to limestone, except that the precipitate was difficult to filter from a cold solution. Spilsbury[73] mentions that the precipitate obtained by treating copper solutions with burned lime was "flocculent and slow to settle." Gahl[74] considers working up a precipitate from copper solutions obtained by use of burned lime as "almost hopeless technically," while the precipitate obtained from the same solution by use of limestone is granular and easily filtered. Millberg[75] uses milk of lime to purify copper sulphate solution, but says that "to get better results in filtration of the residue of basic sulphate certain points are to be observed, in particular the concentration of the milk of lime, the rate of addition of the same to the liquor, and finally the temperature of the liquor, to obtain a finely granular precipitate which can then be filtered easily and with small pressure."

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[73] Spilsbury, E. G., Limestone precipitation of weak copper solutions: Eng. and Min. Jour., vol. 102, 1916, p. 870.

[74] Gahl, Rudolf, Limestone precipitation of weak copper solutions: Eng. and Min. Jour., vol. 102, 1916, p. 1026.

[75] Millberg, Karl, Abröstung und Extraktion von kupferhaltigen Kiesabbränden ohne chlorierende Röstung: Chem. Ztschr., Jahrg. 31, 1907, pp. 1143–1145.

Through the courtesy of Ashio mine officials and the kind assistance of Prof. Gaichi Yamada, of the department of mining and metallurgy, Kyoto Imperial University, a more recent report on the use of lime in differential purification of impure copper sulphate solutions at the Ashio mine is available than that cited earlier in this paper (p. 5). The report transmitted by Professor Yamada follows:

> The differential purification process was discarded in 1914, because of the difficulties in filtration, drying, and transportation. In the earlier practice, precipitates from settling ponds were pumped up to sand-filtering ponds and dried to 91 to 95 per cent moisture content by natural drying. Filtering capacity of sand-filtering ponds of 1,224 square feet area was about 40 to 45 cubic feet of solution per minute. As this filter bed was soon choked up by precipitates, it was necessary to scrape out the precipitates and renew the sand filter once a week.
>
> At present this process is again being investigated at the Ashio mine. The results of preliminary investigations follow:

Mine-water composition, grams per liter

	Example 1	Example 2
Copper	0. 0233	0. 02305
Iron	. 07803	. 10868
Total H_2SO_4	. 73570	. [illegible]
Free acid	. 06410	. 04576
Alumina	. 05973	. 06725
Manganese	. 01756	. 01802
Silica	. 03920	. 07140

> The composition varies with the season and rainfall. The average copper content is over 0.03 gram per liter. The results of experiments with differential precipitation, using different amounts of lime, follow:

TABLE 5.—*Differential precipitation experiments*

Series 1

	Lime used per liter, per cent of theoretical amount					
	50	60	70	80	90	100
Total Cu gram per liter	0. 02037	0. 02223	0. 02037	0. 02037	0. 02176	0. 02246
Cu in precipitate do	. 00046	. 00417	. 01250	. 01991	. 02130	. 02223
Cu in filtrate do	. 01991	. 01806	. 00787	. 00046	. 00046	. 00023
Cu in precipitate per cent	2. 3	18. 8	61. 4	97. 7	97. 9	99.
Total Fe gram per liter	. 09598	. 09649	. 09700	. 09703	. 09699	. 09702
Fe in precipitate do	. 08790	. 09043	. 09245	. 09400	. 09447	. 09500
Fe in filtrate do	. 00808	. 00606	. 00455	. 00303	. 00252	. 00202
Fe in precipitate per cent	91. 6	93. 7	95. 3	96. 9	97. 4	97. 9

TABLE 5.—*Differential precipitation experiments*—Continued

Series 2

	Lime used per liter, per cent of theoretical amount						
	40	50	60	70	80	90	100
Total Cu .... gram per liter	0.0286	0.0270	0.0241	0.0281	0.0304	0.0303	0.0304
Cu in precipitate .... do	.0011	.0017	.0039	.0107	.0253	.0292	.0298
Cu in filtrate .... do	.0275	.0253	.0202	.0174	.0051	.0011	.0001
Cu in precipitate .... per cent	3.8	6.3	16.2	38.1	83.2	96.4	98
Total Fe .... gram per liter	.0892	.0956	.0928	.0924	.0903	.0898	.0908
Fe in precipitate .... do	.0673	.0846	.0861	.0867	.0872	.0872	.0882
Fe in filtrate .... do	.0219	.0110	.0068	.0058	.0031	.0026	.0026
Fe in precipitate .... per cent	75.4	88.5	92.8	93.8	96.6	97.1	97.1

The Ashio officials decided from the above that the best proportion of lime to precipitate iron for their purposes is about 50 per cent of the theoretical amount.

The free settling rate of the precipitates was tested by the method of R. T. Mishler,[76] with the following results:

Free settling rate of precipitates

Grade	Average	Minimum $\frac{60D^a}{T}$	Grade	Average	Minimum $\frac{60D^a}{T}$
	Ft. per hr.	*Ft. per hr.*		*Ft. per hr.*	*Ft. per hr.*
1.050	3.6	3.3	0.821	7.7	6.6
.950	6.9	5.1	.471	5.3	4.0
.860	7.0	5.4	.427	3.5	2.6
.778	7.0	5.3	.386	3.2	3.0
.704	6.1	4.1	.349	2.2	1.7
.636	8.5	6.1	.311	1.4	.8
.576	6.4	5.4	.286	.9	.6

[a] D is depth of clear liquid found per foot of depth, in feet; T is duration of test in minutes.

DOLOMITE

Dolomite acts on the constituents of the copper solution exactly in proportion to its $CaCO_3$ content. Magnesite has no apparent effect, as the amount of oxidation of ferric iron taking place during the aeration with magnesite would be obtained in that time by simple aeration without added substance.

CALCINED LOW-GRADE COPPER ORE

Low-grade copper ore, if calcined at 800° C., removes a small percentage of iron and aluminum when heated with the aerated solutions, but very little when aerated cold. When the ore had been calcined at 600° C., there was more of each impurity in the final solution than in the original. This bears also on the proposition of purifying leach solutions by running them back over dumps of fresh ore.

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[76] Mishler, R. T., Methods for determining the capacities of slime-thickening tanks: Trans. Am. Inst. Min. Met. Eng., vol. 58, 1918, pp. 102–125.

Original from UNIVERSITY OF MICHIGAN

Large-scale attempts to control the building up of impurities in leach solutions thus have sometimes resulted in purification at first, but the impurities built up in the solutions eventually despite the treatment. This was observed at Ajo[77] and in a series of leaching-test runs made by the writers on pyrite calcine with ferric sulphate solutions.

COPPER CARBONATE

Copper carbonates precipitate iron and aluminum from copper sulphate solutions, but the precipitates are very difficult to filter and slow to settle. When malachite aerated only 11½ hours was used, the precipitated hydrates settled less than one-half inch after four months' standing. This corresponds with the directions given by J. S. Ross,[78] in which copper sulphate solutions are boiled with copper carbonate ore to neutralize them, but CuO is added and the solution aerated "to facilitate separation of the precipitated impurities." If copper carbonate ores are used for the bulk of the neutralization, the addition of a more basic substance such as copper oxide or limestone is necessary to flocculate the precipitate to filterable condition.

The investigations of Wolman and Hannan[79] and of Holderer[80] show that the "reaction" (hydrogen ion concentration) of the liquid is very important for the filtration of a pulp, as it controls the size of precipitated particles and the positive or negative charge on the filter medium and particles. Temperature affects the pH of the solution and the rate of coagulation, hence the filterability of pulps.

CHRYSOCOLLA AND CUPRITE

Chrysocolla and cuprite have very little value as hydrolytic agents, chrysocolla because of its very slight effect on the solution in spite of the large amount of unchanged ore still present in the residue, and cuprite because of the immediate reduction of all ferric iron present to ferrous. The time and energy loss in reconverting this added ferrous iron to ferric far outweighs any other advantages offered by cuprite.

RUNS IN STONEWARE CROCK

The work up to this point had been done in glass cylinders with porous bottoms (filtros, alundum, or canvas), with aeration through the bottom. The volume of the solutions was so small that no attempt was made to sample runs in progress, but the whole run was filtered, and solution and precipitate were analyzed for the results. A certain amount usually settled to the bottom of the cylinder in spite of vigorous aeration, with accompanying loss of copper in the precipitate. In an attempt to better these two conditions a series of runs was made with a 12-liter stoneware crock that contained 8 liters of solution which was aerated vigorously by air introduced through a canvas sack at the bottom of the crock. The canvas was stretched over the upper sixth of a 2,500-c.c. acid bottle, which had been cut off near the neck, and was tied tightly around the neck of the bottle. The air was introduced by a glass tube through a rubber stopper in the neck of the bottle.

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[77] Morse, H. W., and Tobelmann, H. A., Leaching tests at New Cornelia: Trans. Am. Inst. Min. Eng., vol. 55, 1916, p. 832.

[78] Ross, J. S., Copper sulphate: Chem. Abs., vol. 14, 1920, p. 2974; Improvements in obtainment of sulphate of copper from ores containing copper, British Patent 143,973, June 7, 1920.

[79] Wolman, Abel, and Hannan, Frank, Further observations on pH in natural waters: Chem. and Met. Eng., vol. 25, 1921, pp. 502–506.

[80] Holderer, Maurice, Recherches sur la filtration des enzymes, Thesis, University of Paris. 1911.

The results of these runs are shown in the following table:

TABLE 6.—*Runs in large crock at 20° C., air agitation, —80-mesh limestone with copper sulphate solution of composition as in Table 3*

Run No.	Limestone used	Time of aeration	Amount precipitated				Notes
			Fe'''	Fe''	Al	Cu	
	Per cent	*Hours*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
119	72.9	75	83.6	82.5	50.6	8.9	Flat bottom in crock.
151	72.0	48	......	80.8	......	......	Run to show effect of excess Cu (double that in run 119) on Fe'' oxidation.
153	72.6	68	......	28.6	......	2.4	Effect of half as much Cu as in run 119 on Fe'' oxidation. Cone bottom in crock, but some settling of precipitate.
154	72.6	46	......	43.9	......	.0	Check on run 153, with better agitation.
155	71.6	30	......	13.3	......	......	Effect of diluting solution of run 119, 50 per cent.
157	Air alone	5	No oxidation				To see if oxidation took place in solution with 1.4 per cent acid by air alone.

The results show that with proper agitation ferric iron and aluminum can be precipitated from copper sulphate solutions with no loss of copper. In run 119 the bottom of the crock used was flat, there was some settling of the precipitate and limestone in the corners of the bottom, and 8.9 per cent of the copper was precipitated. In run 153 this was remedied to some extent by building an inverted cone of cement, covered with paraffin, in the bottom of the crock; it reduced the copper loss to only 2.4 per cent with the same proportion of limestone. Increasing the rate of agitation slightly in run 154 completely corrected the loss of copper and increased the amount of ferrous iron oxidized during the time. The amount of ferric iron precipitated was not determined, because the runs were made primarily to determine the rate of oxidation of ferrous iron; but from preceding results, ferric iron and aluminum would be 85 to 95 per cent precipitated when ferrous iron was 44 per cent oxidized.

The results of the runs in reoxidation will be taken up in connection with oxidation runs made in the rotary aerator.

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RUNS IN ROTARY AERATOR

From all the preceding work, it was evident that ferric iron and aluminum can be precipitated satisfactorily from copper solutions and ferrous iron oxidized by aeration. The removal of ferrous iron by this method is very slow, as the results show. To attempt to hasten this oxidation and the flocculation of colloidal solutions, the authors tried working at higher temperatures and breaking up the air supply into smaller bubbles. Hanley [81] found that fine-bubble aeration greatly increased the rate of oxidation of ferrous iron over that of coarse-bubble aeration. The authors also used a suggestion from Greenawalt [82] for producing fine-bubble aeration combined with efficient aeration.

APPARATUS

The principle of the apparatus is that the air for oxidation issues from the ends of the arms of the mechanical stirrer, and is thereby broken up into fine bubbles. The authors used tubes of hard rubber, of Tobin bronze, of copper, and finally of glass as stirrer arms. The reaction vessels, first of glass, then of stoneware, then of lead, were of 4 liters capacity, but were run with 3 liters to allow for stirring and aeration. The reaction tanks were jacketed with asbestos and heated with small electric hot plates, and the heating current was controlled by ammeters and rheostats. It was not difficult to keep the temperature of the solutions constant within a degree up to 85° C. Evaporation was controlled by frequent addition of water at the temperature of the run, to make up for that lost. The depth of the solution in the tank was measured to within a millimeter, and the solution was made up to the measured depth, the stirrer being stopped a moment for the purpose. The rate of air flow was measured by flow meters calibrated for the purpose. The volume of the solutions was such (3,000 c. c.) that removal of 5 c. c. samples for analysis never had any apparent effect on the results, only a few samples being necessary during a run.

Stirrers that contained copper or zinc were attacked by the solutions that were acid and contained ferric iron. This action, of course, distorted the results of those runs, so that the stirrers were replaced by similar ones made wholly of glass and the runs were repeated. Hard-rubber stirrers were chemically satisfactory, but broke more easily than those of glass, which lasted for many runs. The glass tanks were discarded because they could not stand the heating, and those of stoneware because most of them were slightly porous. Lead tanks with glass stirrers were entirely satisfactory.

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[81] Hanley, H. R., Electrolytic zinc methods: Min. and Sci. Press, vol. 121, 1920, pp. 795–804.

[82] Greenawalt, W. E., Oxidation of ferrous salts by atomized air in acid solution thought practicable: Eng. and Min. Jour. Press, vol. 114, 1922, p. 933.

With this apparatus an attempt was made to see how the oxidation of ferrous iron could be accelerated. Previous work had shown that iron and aluminum could be precipitated without loss of copper, so, with that phase of the matter settled, the oxidation of ferrous iron was studied, with losses of copper in precipitates (which were sometimes very large), a matter secondary to the main purpose of determining the rates of oxidation of ferrous iron.

COMPOSITION OF SOLUTIONS

The solutions used were of the composition of those most used in previous work: Cu 30 grams per liter, ferrous and ferric iron 5 grams per liter each, Al 10 grams per liter, and free acid 15 grams per liter, except where changed for determining the effect of absence or excess of a constituent.

RESULTS OF RUNS IN ROTARY AERATOR

Results of rotary aerator runs are given in Table 7.

TABLE 7.—*Rotary aerator runs, with —80-mesh limestone added*

Runs at 20° C.

Run number	Limestone	Time of aeration	Amount precipitated				Notes
			Fe‴	Fe″	Al	Cu	
	Per cent	*Hours*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
158	100.7	5	100	54.3	------	12.0	Run with no aluminum present.
160	102.3	6	100	66.2	79.2	15.8	2.5 g/l Al added to sol'n of 158.
161	101.9	6½	100	32.1	46.4	29.8	5.0 g/l Al added to sol'n of 158.
163	101.6	6	100	29.2	85.5	36.5	7.5 g/l Al added to sol'n of 158.
165	102.3	6¼	100	35.2	------	------	Check on 158, with 60-mesh limestone. No Al in sol'n.
179	107.8	3	100	100	------	------	First pilot run at 75° C.
185	78	21	100	100	------	------	Probably oxidation complete in shorter time, as analysis made after all-night run.
Higher-temperature runs							
221	59.6	7	100	98.1	------	20.4	No Al in orig. sol'n. (temp. 85°).
222	95.6	6	100	99.5	100	65.6	Temp., 85°.
223	106.4	6	100	95.0	100	86	Temp., 60°.
224	96	5½	100	55.5	------	------	
		12	------	97.4	------	0.4	Temp., 60°.
					Final precipitate.		

Runs 158 to 163 show the specific effect of Al in slowing the oxidation of ferrous iron, even when the solution is neutralized by limestone. Run 165 shows how much slower the oxidation goes when 60-mesh limestone is substituted for 80 mesh. Run 185 was a comparison of the rotary aerator oxidation with that in the glass cylinder runs, using the same solution and same proportion of limestone. It is evidently faster in the rotary aerator, although just how much faster the experiment does not show.

The higher temperature runs show that the oxidation of ferrous iron is very much faster under these conditions and also that a very much smaller proportion of limestone precipitates iron and aluminum completely at high temperature than at room temperature. Where 78 per cent was necessary for the complete precipitation of iron and aluminum at room temperature, 59.6 per cent at 85° C. not only precipitated all the iron but also 20.4 per cent of the copper.

Tests of the filtrate in the high-temperature runs, from time to time during a run, showed that the acidity of the solution was increasing and also that the copper entrained in the precipitate was decreasing. In run 224 acid was added very gradually with frequent tests after the iron was all down to see if all the copper could be redissolved without dissolving the iron. It was impossible to get all the copper out of the precipitate at any acidity at which all the iron stayed precipitated. The iron began to redissolve after the concentration of copper in the precipitate had been reduced to 0.4 per cent.

Similar precipitates have been worked up by smelting, as at the Ashio mine[83] and in Corbould's process,[84] with his "first purification precipitate" by leaching with ferric sulphate,[85] or with ammonia,[86] or with ferrous chloride and sodium chloride, as in Bunzel's process.[87]

A number of runs were made with the rotary aerator with a ferrous sulphate solution of 20 grams Fe'' per liter to start and ferric iron, copper, aluminum, zinc, and free acid added later. The rate of aeration was fixed, but the temperature was varied in steps from that of the room to 85° C. The object was to see how the rate of oxidation of ferrous iron was affected by the added substances, of which the free acid was, of course, the most important since it is practically always present in solutions containing ferrous iron that is to be oxidized.

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[83] Richards, J. N., Treatment of mine water from the Ashio copper mine: Trans. Am. Inst. Min. Eng., vol. 43, 1912, pp. 464–467.

[84] Corbould, W. H., Corbould's copper-extraction process: Min. Mag., vol. 25, 1921, pp. 381–385.

[85] Millberg, Carl, Kupfervitriolgewinnung aus Kiesabbränden und minderwirtigen Kupfererzen: Chem. Ztschr., Jahrg. 30, 1906, pp. 511–513.

[86] Burbidge, P., A proposed copper-metallurgical process: Proc. Aus. Inst. Min. Met., vol. 42, 1921, p. 11.

[87] Bunzel, Hugo, Verfahren zur Abscheidung des Kupfers aus kupferhaltigen Laugen. German Patent 366187, Dec. 30, 1922.

TABLE 8.—*Rotary aerator runs with ferrous sulphate solutions 20 g/l Fe''' originally; 3 liters of air per minute*

Run No.	Temperature	Time of aeration	Oxidation velocity constant	Notes
	°C.	*Hours*		
197	18	27¼	0.000047	20 g/l Fe''' added.
198	18	24½	.0000073	Neutral $FeSO_4$ alone.
199	18	24½	.0000086	10 g/l sulphuric acid added.
200	40	9½	.0000041	20 g/l Fe''' added.
201	40	9¼	.000026	Neutral $FeSO_4$.
203	65	6½	.0000147	20 g/l Fe'''.
204	65	6¼	.0000212	10 g/l free acid added.
205	50	6	.0000145	Neutral ferrous sulphate alone.
206	85	5	.0000321	Fe''' 20 g/l added.
207	50	5½	.0000085	10 g/l free sulphuric acid added.
208	65	5½	.0000070	Neutral ferrous sulphate alone.
209	18	15½	.0000060	20 g/l Zn as sulphate added.
210	18	15	.0000011	20 g/l Al as sulphate added.
211	50	5	.0000068	Do.
211a	65	5¼	.0000126	Do.
212	65	5½	.0000194	20 g/l Zn as sulphate added.
212a	50	5	.0000126	Do.
213	85	12½	.0000922	Neutral ferrous sulphate alone.
214	18	22	.0000017	Neutral ferrous sulphate, check run in Pb jar.
215	50	5	.0000079	Do.
216	65	6	.0000184	Do.
217	18	22	.0000063	20 g/l Cu as sulphate added.
218	65	6	.0000451	Do.
219	50	6	.0000148	Do.
220	85	5	.000119	Do.

REACTION VELOCITIES

The outstanding feature of the reaction velocities in Table 8 is their extreme smallness. The catalytic effect of added Cu is evident here, as it was in Table 6, p. 35, runs 119, 151, and 153; also the negative catalysis by added Al is evident, as in Table 7, runs 158 to 163. The main feature is the comparison of the largest reaction velocity attained in these neutral solutions—that with added Cu at 85° C., of 0.000119—with the value 0.000287 calculated from Table 7, run 179, where the reaction proceeds at 75° C. in the presence of excess limestone. The velocity is nearly three times as great.

In general, the velocities of oxidation of ferrous iron either in acid or neutral solution, with any of these metals for catalysts, are too slow to be of practical value. For any reaction to be so, the oxidation of ferrous iron by simple aeration must go on in less acid or even in alkaline solution. This leads to excessive losses of Cu in the precipitate (up to 86 per cent as in Table 7, run 223). The method of recovering precipitated Cu by gradual acidification of the final reaction mixture after the ferrous iron has been oxidized to ferric and precipitated would allow the ferrous iron to be oxidized within reasonable time. The copper might be recovered by smelting or by other methods of extraction, such as by ammonia, ferrous chloride, or ferric sulphate; but whether lime, limestone, or more active copper compounds are used, any practical method for precipitating iron and aluminum from copper sulphate solutions must include extraction of copper from the final precipitate. The precipitated iron and aluminum hydroxides are not easily redissolved in weak acid solutions after a period of standing.

IMPROVEMENTS IN TECHNICAL PROCEDURE

As a suggested improvement in technical procedure, it would probably be best to purify impure copper sulphate solutions by neutralizing free acid by the addition of some copper compound such as carbonate or oxide, and to save as much of the sulphate radical as is desirable. The solution should then be heated to 60° C. if quick oxidation with small volume of solutions is desired. and limestone should be added to bring the acidity of the solution below the point possible if copper compounds were used. A little of the copper is precipitated, and the ferrous iron present oxidized by fine-bubble aeration with preheated air. After the ferric precipitate is all down and flocculated enough, acid is added cautiously until the copper is out of the precipitate and iron just begins to dissolve. With a large volume of more dilute solutions, it would probably be cheaper to aerate at lower temperature in Pachuca tanks, with the same addition of limestone to bring the acidity down during oxidation. If manganese dioxide can be obtained cheaply and the presence of a trace of manganese in the resulting solutions is not detrimental, the time and expense of oxidation can be greatly reduced by the addition of minus 100-mesh manganese dioxide, both for its direct oxidizing effect and the catalytic effect on oxidation by aeration already mentioned. The acidity required can be determined roughly by the usual method of titration with indicators, using a filtered and diluted portion of the solution; or it can be found accurately by the electrometer method.

Research at the Pacific and Tucson stations of the Bureau of Mines has shown that the oxidation by aeration of ferrous to ferric iron in solution is very much more rapid when small amounts of sulphur dioxide are mixed with the air before entering the reaction solution. In the hope that the oxidation of ferrous iron might be hastened similarly in the impure copper sulphate solutions tested, trial was made of the rate of oxidation by a sulphur dioxide-air mixture whose concentration was that found efficient with ferrous sulphate alone, or the synthetic impure copper sulphate solutions used in most of the previously described work, or with leach solutions from the Mountain Copper Co. that contained the impurities already worked with plus 5 to 7 grams per liter of zinc. It was found that at room temperatures there was no oxidation of ferrous iron whatever in the presence of the amounts of copper occurring in this sort of solution. Even small amounts of copper with sulphur dioxide-air mixtures were found to exert a marked negative catalysis on the rate of oxidation of ferrous iron in solution.

Additional runs with sulphur dioxide-air mixtures were made at 50° C., a temperature showing an optimum rate of oxidation of ferrous iron in solution alone. The rotary aerator was used for these runs. The rate of oxidation was found to be almost identical with that obtained in Table 8, run 205, where only air was used for the oxidation of ferrous sulphate alone, and slower than the rate found in Table 8, run 219, where air alone was used for the oxidation of a similar copper sulphate-ferrous sulphate solution, all three runs being at 50° C.

That addition of limestone to reduce acidity during oxidation with the sulphur dioxide-air mixture might increase the rate of oxidation was another possibility. On trial, the addition of limestone of minus 80-mesh during the run was found to be without effect, there being no oxidation whatever of the ferrous sulphate with sulphur dioxide-air mixture in the presence of copper at room temperatures, even when considerable amounts of limestone were added.

EXPERIMENTAL PURIFICATION OF COPPER SULPHATE SOLUTIONS ON COMMERCIAL SCALE IN COOPERATION WITH MOUNTAIN COPPER CO.

Work was done on the purification of two kinds of solutions, the "heads" solution of the bluestone plant, containing as an example Cu 64.88 grams per liter, FeO 6.60 grams per liter, Fe_2O_3 0.30 gram per liter, Zn 2.80 grams per liter, and H_2SO_4 11.76 grams per liter, and the "foul" solution of the bluestone plant, resulting from three or more successive evaporations and crystallizations of the "heads," and containing as an example Fe'' 18.22 grams per liter, Fe''' 5.90 grams per liter, Cu 34.40 grams per liter, and H_2SO_4 117.7 grams per liter.

When the Fe'' concentration reaches about 25 grams per liter the ferrous iron causes trouble because the sulphate crystallizes out with copper sulphate. The problem was to remove this ferrous iron without prohibitive loss of copper.

Hoffmann's method [88] was tried, first on a small scale in the laboratory, and then on a commercial scale at the bluestone plant on the foul solutions, because the work in the laboratory showed that the "heads" solution was extremely slow to oxidize in its original concentration, although on its dilution to below 20° B. the oxidation of ferrous iron and precipitation as ferric proceeded well. This agrees with the findings of Millberg,[89] who says "We found in this work that the concentration of the solution was of importance, and that the oxidation went most rapidly in dilute solution, and with maximum strength of 18° to 20° B." On account of the much larger volume of solutions that would have to be handled if the heads solution were purified (because the foul solution results from three or more concentrations of the heads solution by evaporation), especially if the heads solution were diluted for purification, which would entail the evaporation of large amounts of water, no work was done on the heads solution at the plant. In the laboratory it was found that for some unexplained reason the foul solution could be purified in its original concentration and that diluting it hastened the reaction only slightly.

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[88] Greenawalt, W. E., Hydrometallurgy of copper. 1912, pt. 2, p. 434.

[89] Millberg, Carl, Kupfervitriolgewinnung aus Kiesabbränden und minderwertigen Kupfererzen: Chem. Ztschr., Jahrg. 30, 1906, p. 511.

At the plant, therefore, two runs were made on undiluted foul solution, and one with the solution diluted with its own volume of water, to specific gravity 1.10. The solutions were heated in the tank used for dissolving the copper oxide made by roasting cement copper. For the first run, in addition to the "propeller" agitator already in the tank an aeration pipe was introduced leading across the diameter of the tank at a depth of about 2 feet, perforated every 1½ feet with one-eighth-inch holes pointing downward. For the next two runs there was introduced outside the ends of the agitator arms an additional air pipe, perforated as before and lying on the bottom in a single coil around the outer edge of the tank.

The solutions were heated by live steam from a pipe dipping about 18 inches into the solution. The temperatures ranged from 75° to 90° C., averaging about 85° C. Condensation of steam always caused the solutions to increase slightly in volume.

Chemical control was by determinations of acidity and of ferrous iron. The acidity was determined by titration of 10 c. c. portions of the solution diluted to about 250 c. c., with N/2 KOH, using a methyl orange indicator. The ferrous iron was determined by titration of 10 c. c. portions of the solution, diluted to 150 c. c. and acidified with sulphuric acid, against N/10 $KMnO_4$. The air electrode was introduced in the third run to obtain check data, but was not used for control. The course of the runs is shown in the following table:

TABLE 9.—*Purification runs on commercial scale*

Run No.	Per cent of equivalent CuO used	Per cent of original Fe'' oxidized in—							
		2 hours	4 hours	6 hours	8 hours	10 hours	12 hours	14 hours	16 hours
166	101.3	−6.4	1.75	10.35	11.35	20.9	26.25	30.8	35.1
[a] 172	133.5	−5.7	−2.3	4.66	18.00	30.3	42.6	55.6	66.7
173	92.2	−19.5	−13.85	−4.6	.3	8.22	14.7	23.4	32.8

[a] Dilute solution.

The rate of oxidation in run 172 is substantially the same as in the other two, because removal of the same actual amount of Fe″ would have double the percentage effect in the solution of half the strength. The copper added by the dissolving of copper oxide in neutralizing free acid and precipitating iron increased the copper sulphate concentration so that on settling the solution was ready at once to be run into the crystallizing tanks for a crop of bluestone. The degree of purification attained would permit at least one evaporation for another crop of bluestone crystals before further difficulty with ferrous sulphate crystallizing out would occur.

The runs were continued beyond this point to determine the limit of removal of ferrous iron, and it was found that the rate of oxidation became slower and slower and that several days' aeration did not remove the last trace of ferrous iron.

CONCLUSIONS

The conclusions reached are as follows:

1. Practically all the ferrous iron can be oxidized in foul bluestone solutions, either in original strength or diluted, by aeration at 70° to 80° C.

2. There is no advantage in diluting the solution. The original solution oxidized at practically the same speed as the diluted solution.

3. There is no necessity for fine grinding of the copper oxide used for precipitation of the iron after the solution is neutralized by addition of mill-run copper oxide. The finely ground (—200-mesh) copper oxide used in run 173 increased the rate of oxidation very slightly, but not enough to pay for the extra trouble of grinding finer than 70 mesh.

4. The precipitate settles well, so that the clear solution can be siphoned off after it has stood overnight and is still warm. A filter press or thickener is therefore not necessary.

5. The percentage rate of oxidation is considerably slower than that found by Hofmann, or by Pope and Hahn, who worked with dilute solutions approximating the composition of the diluted "heads" solution, but the rate of removal of iron per hour is about the same. These solutions contain a great deal more ferrous iron than those worked with by the persons named above, and at the same rate of actual oxidation should take much longer to have the ferrous iron completely or sufficiently removed.

6. The rate of oxidation and removal becomes very much slower as the reaction approaches completion, so that the complete removal of the iron would take an entirely impracticable time.

7. The iron remaining in the solution continues to oxidize and precipitate after aeration is stopped, so that for crystallization of clean bluestone from the purified solutions it is necessary to acidify before running the solutions to the crystallizing tanks. The amount of acid necessary to prevent the further oxidation and precipitation of the iron is about 20 pounds of chamber acid per 150 cubic feet of solution. Theoretically, acid in the strength of N/100 would keep ferric iron in solution, but that strength makes no allowance for other possible acid consumers in the foul solution.

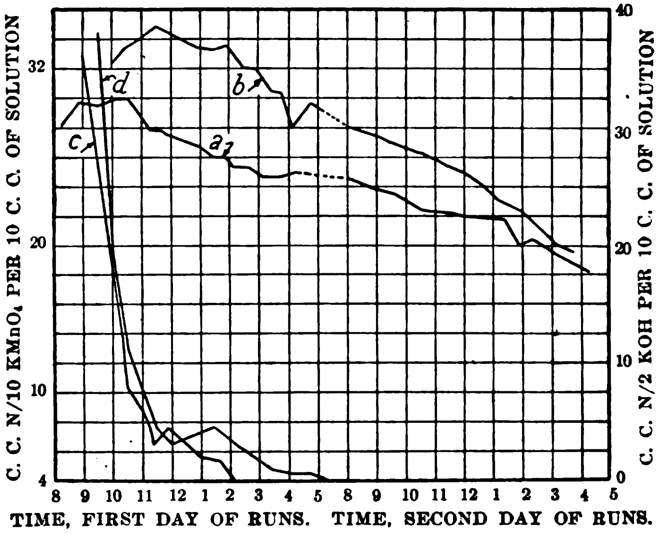

FIGURE 5.—Rate of neutralization and oxidation in two runs: *a*, Rate of oxidation of ferrous iron by aeration of commercial bluestone solution at 85° C., in terms of cubic centimeters of N/10 $KMnO_4$ per 10 c. c. of solution; *b*, same as *a*, with minus 200-mesh copper oxide as hydrolytic agent; *c*, rate of neutralization of *a*, in terms of N/2 KOH per 10 c. c. of solution; *d*, same as for solution of *b*. The "knicks" in *a* and *b*, as well as the initial rise in Fe'', are always due to the reduction of Fe''' present by the Cu_2O in added copper oxide. The points in the lower ends of the neutralization curves are doubtful on account of the extreme difficulty of determining acidity in complex solutions by titration.

8. The oxidation goes with equal rapidity after neutralization, without running the agitator. When a shallow dissolving tank is used, the added cement copper oxide tends to settle in the corners and form a hard cake if the agitator is not run. This would not happen if a deep, narrow tank with cone bottom were used, with aeration from the bottom.

9. On account of the neutralization of a considerable amount of free acid by the CuO added to neutralize the solution, the resulting purified solution is ready for crystallization of copper sulphate at once, and the solutions purified in the runs on undiluted foul solution

could be further evaporated and another crop of crystals obtained from them at least once before they again needed purification if the solution were handled by itself. In practice, the mother liquors would be mixed with others and the foul solutions treated in economical quantities when enough had accumulated for a run.

10. The basic ferric sulphate formed in the purification would be a source of gain, on account of its solvent effect, if returned to the leaching tanks after dissolving to recover entrained and undissolved copper.

The accompanying graphs (Fig. 5) show the rate of neutralization and oxidation in the two runs. The rise in Fe'' concentration at first is due to the presence of cuprous oxide in the roasted cement copper used, and each time cement copper was added there was a temporary rise in Fe'', as shown by " knicks " in the curve.